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Pilot-Scale Incineration Test Burn of TCDD-Contaminated Trichlorophenol Production Waste

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PILOT-SCALE INCINERATION TEST BURN OF TCDD-CONTAMINATED TRICHLOROPHENOL PRODUCTION WASTE

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For

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
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A series of three tests directed at evaluating the incinerability of the toluene stillbottoms waste from trichlorophenol production previously generated by the Vertac Chemical Company were performed in the Combustion Research Facility (CRF) rotary kiln incineration system. This waste contained 37 ppm 2,3,7,8-TCDD as its principal organic hazardous constituent (POHC). Flue gas 2,3,7,8-TCDD levels were less than detectable at all locations sampled. Corresponding incinerator destruction and removal efficiencies (DREs) were greater than 99.9997 percent, based on individual sampling train analyses. By analyzing combined extracts from four simultaneous sampling trains, it was concluded that 2,3,7,8-TCDD DRE was indeed greater than 99.9999 percent. These results suggest that incineration of the Vertac waste is capable of achieving the required DRE and should be considered a treatment option for this waste.

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FOREWARD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report will be useful to EPA's OSWER, Regional Office RCRA and CERCLA Permit Writers, State and Local Environmental Offices.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

A series of three tests directed at evaluating the incinerability of the toluene stillbottoms waste from trichlorophenol production previously generated by the Vertac Chemical Company were performed in the Combustion Research Facility (CRF) rotary kiln incineration system. The waste contained 37 ppm 2,3,7,8-TCDD as its principal organic hazardous constituent (POHC). Flue gas 2,3,7,8-TCDD levels were less than detectable at all locations sampled. Corresponding incinerator destruction and removal efficiencies (DREs) were greater than 99.9999 percent. These results suggest that incineration of the Vertac waste is capable of achieving the required DRE and should be considered a treatment option for this waste.

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ACKNOWLEDGMENTS

The actual incineration tests, results of which are reported in this document, were performed by Versar, Inc., Southern Operations, during September 1985, while under contract to EPA to operate its Combustion Research Facility in Jefferson, Arkansas. Acurex Corporation has the current contract to operate the facility, and thus the responsibility for reporting results of these tests which, again, were performed by Versar.

EXECUTIVE SUMMARY

A series of incineration experiments was performed with the Vertac Chemical Company's toluene stillbottoms waste from trichlorophenol production. This waste is one of the more well known of the dioxin-contaminated wastes presently in existence. Samples of the waste tested in this study contained an average of 37 ppm, 2,3,7,8-TCDD (37 µg/g). The primary objective of these tests was to evaluate the incinerability of the Vertac toluene stillbottoms waste by determining whether 99.9999 percent destruction and removal efficiency (DRE) of the 2,3,7,8-TCDD could be achieved, as required by current regulations.

The results of the tests suggest that incineration should be considered a viable disposal method for this stillbottoms waste, given that appropriate safeguards are employed. The data in this study confirm that incineration under the conditions existing in the CRF pilot incinerator system for these tests is capable of achieving 99.9999 percent dioxin DRE.

The test program performed consisted a total of four trial burns performed in September 1985. These trial burns consisted of the following:

- A blank burn with the incinerator fired with auxiliary fuel (propane) only to establish background emission levels of pollutants of concern

- A miniburn of short duration (4 hours) with waste fired at nominally 17 kg/hr (38 lb/hr) to demonstrate the ability to feed and incinerate the waste and to gain experience with the sampling protocols specified

- Two full waste test burns of nominally 10-hour duration with the waste fired at about 10 and 18 kg/hr (22 and 39 lb/hr) to specifically address the test objectives

All tests were performed in the rotary kiln incineration system at the CRF with kiln temperatures maintained above 980°C (1800°F) and afterburner temperatures maintained above 1110°C (2030°F). Nominal gas residence times were 5 to 6 sec in the kiln and about 2.5 sec in the afterburner.

The sampling protocol for the test program included the following:

- Measuring flue gas O_2, CO_2, CO, and NO_x levels at the afterburner exit and in the stack using continuous emission analyzers

- Sampling for flue gas particulate and 2,3,7,8-TCDD levels at the kiln exit, the afterburner exit, downstream of the scrubber system (the E-duct), and in the stack downstream of the system's backup air pollution control system (a carbon bed absorber followed by a HEPA filter) using Modified Method 5 (MM5) trains. In general two trains were simultaneously operated at the kiln exit, the afterburner exit, and the stack, and four trains were simultaneously operated at the E-duct location.

- Measuring flue gas HCl levels at the E-duct location using a continuous emissions analyzer

- Obtaining grab samples of the composite kiln ash, composite scrubber blowdown, and the waste feed

The analysis protocol applied to samples obtained via the above included:

- Analyzing the waste feed and MM5 train samples for 2,3,7,8-TCDD

- Analyzing the kiln ash and scrubber blowdown for 2,3,7,8-TCDD and the polychlorinated dibenzo-p-dioxins (PCDDs) and the polychlorinated dibenzofurans (PCDFs) of chlorine substitution 4 through 8

- Analyzing the waste feed and the scrubber blowdown for the organic and trace element priority pollutants

All tests were performed at high excess air, flue gas O_2 was in the 10 to 17 percent range in the afterburner exit and in the 13 to 17 percent range in the stack. CO emissions were always low, <10 ppm, as were NO_x levels, <30 ppm. Unfortunately, the continuous monitoring data are not complete, since problems with continuous monitor failure occurred. For the miniburn test, the HCl emission rate was 0.45 kg/hr; for the first full burn test, the HCl emission rate was 0.25 kg/hr. Both of these are less than the CRF permit level of 0.5 kg/hr.

Particulate levels at both the kiln and afterburner exit were quite low (in the several mg/dscm or less range) during the background burn with propane fuel alone, as expected. Flue gas particulate levels for the test with waste feed were highly variable and ranged from several to several hundred mg/dscm. Due to technical and operating factors, accurate particulate measurements could not be made. Further work in this area is needed.

Flue gas levels of 2,3,7,8-TCDD were less than method detection limits at all locations for all tests. The levels at the virtual stack (the sampling point for design parameters) correspond to a DRE of greater than 99.9999 percent. The virtual stack corresponds to the stack of an actual hazardous waste incinerator.

The kiln ash and the scrubber blowdown water from this entire test series was analyzed for tetra- through octa-chloro dibenzodioxins and dibenzofurans. The kiln ash samples were devoid of PCDDs and PCDFs to detection limits ranging from 3 to 40 ppt. Scrubber blowdown samples were devoid of all PCDDs and PCDFs except octa-CDDs which were present at 0.07 ppt. This is not surprising since octa-CDDs are relatively common in environmental samples.

The scrubber blowdown was also analyzed for the organic and trace element priority pollutants. No organic priority pollutant was present in the blowdown at levels greater than 10 ppb. In addition, none of the trace elements were present at concentrations which would cause the blowdown water to be considered EP toxic. Based on these results, the blowdown water would not be considered a hazardous waste.

SECTION 1

INTRODUCTION

A primary function of the Environmental Protection Agency's (EPA) Combustion Research Facility (CRF) is to perform incineration testing of troublesome hazardous wastes to support decisions regarding whether incineration is a proper waste treatment/disposal option. One class of such wastes is those contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD or dioxin).

Since dioxin is an extremely toxic compound, current regulations require that the incineration of dioxin-contaminated wastes result in a destruction and removal efficiency (DRE) of 99.9999 percent. For an incinerator system to be permitted to dispose of dioxin-contaminated wastes it must establish, by way of a trial burn, that it is capable of achieving this level of DRE. However, owing to the expense of performing a trial burn, coupled with public concerns over performing a trial burn in which DRE could conceivably be somewhat less than 99.9999 percent, no commercial trial burns of dioxin-contaminated wastes have yet been permitted. These concerns have been heightened by the fact that dioxin is thought by some to be a product of incomplete combustion (PIC) of dioxin precursor materials, so that an incineration process might not be able to establish 99.9999 percent DRE due to the combined emissions of undestroyed dioxin plus dioxin formed as a result of combustion of other materials.

An example of a well-established, highly dioxin-contaminated waste is the toluene stillbottoms from trichlorophenol production previously generated and currently being stored, pending a decision regarding appropriate treatment/disposal, at the Vertac Chemical Company in Jacksonville, Arkansas. The generator is currently considering onsite incineration in a mobile incinerator system as an avenue for disposal of this waste and wishes to have a permit for a trial burn issued. The CRF was requested to perform a series of test burn experiments of this waste to establish whether the waste could indeed be considered incinerable, i.e., could 99.9999 percent DRE of dioxin be achieved under well-controlled incineration conditions. Results of these incineration tests would in turn be used to support any subsequent permit decision. That is, if 99.9999 percent DRE could be established in the CRF tests, then an actual trial burn in a well-designed mobile incineration system might reasonably be expected to similarly result in the required DRE.

Thus, the primary objective of the tests reported herein was to evaluate the incinerability of the Vertac toluene stillbottoms waste by determining

whether 99.9999 percent DRE could be achieved. However, in that the CRF is itself a permitted hazardous waste disposal facility, the tests also had to address a secondary objective. These tests also represented a trial burn for the CRF. Thus, measurements to establish whether the entire CRF incineration system could achieve required DRE, particulate emissions, and HCl emissions and removal efficiency had to be performed. Casting these tests in the form of a research program to satisfy the primary objective, as well as a regulatory trial burn, to satisfy the CRF permit mandates, was required.

All tests were performed in the CRF rotary kiln incineration system. This system consists of a pilot-scale rotary kiln, fired afterburner, venturi scrubber/wetted elbow, and packed tower scrubber. A redundant control system comprised of a carbon bed and HEPA filter is also in place. The test program performed consisted of a total of four trial burns:

- A blank burn with the incinerator fired with auxiliary fuel (propane) only to establish background emission levels of pollutants of concern
- A miniburn of short duration (4 hours) with waste fired at nominally 17 kg/hr (38 lb/hr) to demonstrate the ability to feed and incinerate the waste and to gain experience with the sampling protocols specified
- Two full waste test burns of nominally 10-hour duration with the waste fired at about 10 and 18 kg/hr (22 and 39 lb/hr) to specifically address the test objectives

All tests were performed during September 1985: the blank burn on September 4, the miniburn on September 9, and the full burns on September 20 and 21. The tests were performed by Versar, Inc., Southern Operations, under EPA contract 68-03-3128, which expired on September 30, 1985. Acurex Corporation has since assumed CRF operation's responsibility, and has, therefore, been charged with the responsibility to reduce and summarize test results.

Results of the tests are summarized in this report. In the following, Section 2 presents a description of the test system and summarizes its operation during the tests. Waste characterization data are also given. Section 3 summarizes the sampling and analysis protocols employed during the tests. Section 4 presents test results. Conclusions from the tests are summarized in Section 5. Quality assurance/quality control (QA/QC) and health and safety aspects of the tests are discussed in Sections 6 and 7, respectively.

SECTION 2

FACILITY DESCRIPTION, WASTE CHARACTERIZATION, AND SYSTEM OPERATION

The test program, which is the subject of this report, was conducted in the CRF rotary kiln incineration system. A description of this system is given in Section 2.1. Section 2.2 discusses waste characteristics and Section 2.3 describes the operation of the system during the tests performed.

2.1 ROTARY KILN INCINERATION SYSTEM DESCRIPTION

The rotary kiln incineration system at the CRF consists of a rotary kiln primary combustion chamber, a fired afterburner, and a primary air pollution control system consisting of a venturi scrubber, wetted elbow, and packed tower scrubber. In addition, a backup air pollution control system (APCD) consisting of a carbon-bed absorber and a HEPA filter is in place. The primary APCD might be considered reflective of what might exist in an actual commercial or industrial incinerator. The backup system is in place to ensure organic pollutant and particulate emissions to the atmosphere are negligible.

A schematic of the system is given in Figure 1. Table 1 summarizes the design characteristics of the main elements of the system.

For these tests, waste was introduced at the feed face through the front face lance with a Durometer type J1-10058-06D double chamber, double diaphragm pump, while auxiliary fuel (propane) was fired through a burner located at the transfer duct end of the kiln. The afterburner was also fired with auxiliary fuel. Waste for feeding was contained in a 950L (250 gal) Tote tank placed on a Weightronic scale so that mass feedrate could be determined.

Combustion gases were continuously monitored for CO, CO_2, O_2, and NO_x using a continuous Bendix Combustion Gas Analyzer system. Readings were taken at the afterburner exit and at the stack location downstream of the ID fan on a cycling basis. Provision also exists for extractive gas sampling in the kiln transfer duct, at the afterburner exit, in the duct between the packed tower scrubber and the carbon-bed absorber (referred to as the E-duct), and at the stack downstream of the ID fan. Sampling protocols used at each location are discussed in Section 3.1. Total hydrocarbon levels were monitored using a Beckman heated total hydrocarbon analyzer upstream and downstream of the carbon-bed absorber on a cyclic basis.

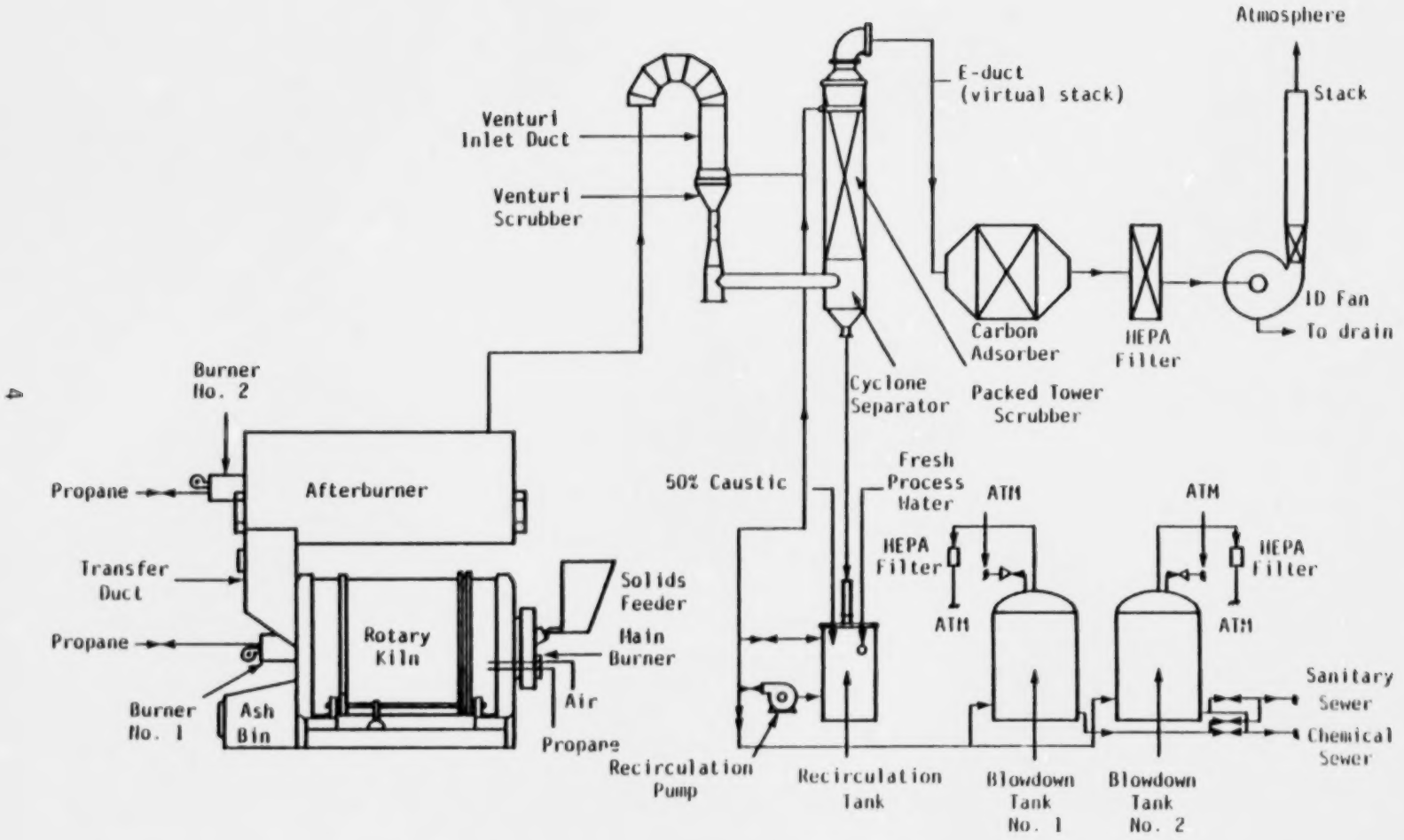


Figure 1. Simplified rotary kiln system schematic.

TABLE 1. DESIGN CHARACTERISTICS OF THE CRF ROTARY KILN SYSTEM

Characteristics of the Kiln Main Chamber		
Length	2.44m	(8 ft)
Diameter	1.22m	(4 ft)
Chamber volume	2.88 m^3	(100 ft^3)
Rotation	clockwise or counterclockwise 0.1 to 1.5 rpm	
Construction	0.63 cm	(0.25 in.) thick cold rolled steel
Refractory	12.7 cm	(5 in.) thick high alumina castable refractory, variable depth to produce a frustroconical effect for moving inerts
Solids retention time	1 hr (at 0.5 rpm)	
Burner	Iron Fireman, model C-120-G-SMG, rated at 530 kW (1.8 MMBtu/hr)	
Primary fuel	Propane	
Feed system	Liquids:	front face, water cooled lance with positive displacement pump
	Semiliquids:	front face, water cooled, lance with double diaphragm pump
	Solids:	Metered twin auger screw feeder
Temperature	900°C (1650°F) maximum operating	
Characteristics of the Afterburner Chamber		
Length	3.05m	(10 ft)
Diameter	0.91m	(3 ft)
Chamber volume	2.096 m^3	(74 ft^3)
Construction	0.63 cm	(0.25 in.) thick cold rolled steel
Refractory	15.24 cm	(6 in.) thick high alumina castable refractory
Retention time	depends on temperature and excess air	
Burner	Iron Fireman, model C-120-G-SMG, rated at 530 kW (1.8 MMBtu/hr)	
Primary fuel	Propane	
Temperature	1200°C (2200°F) maximum operating	
Characteristics of the Air Pollution Control System		
System capacity	Inlet gas flow of 106.8 m^3/min (3773 acfm) at 1200°C (2200°F) and 101 kPa (14.7 psia)	
Pressure drop	Venturi 7.5 kPa (30 in. WC)	
	Packed tower 1.0 kPa (4 in. WC)	
Liquid flow	Venturi 77.2 L/min (20.4 gpm) at 69 kPa (10 psig), tower 116 L/min (30.6 gpm) at 69 kPa (10 psig)	
pH control	Feed back control by NaOH solution addition	

Normally, scrubber blowdown from the primary APCD system is collected in two permanent heat traced tanks as shown in Figure 1. However, for these tests, scrubber blowdown was directed to two temporary storage tanks obtained just for these tests. The combined capacity of these tanks was nominally 26,500L (7000 gal).

2.2 WASTE CHARACTERIZATION

Table 2 summarizes a generic characterization of the toluene stillbottoms waste based on previous data developed by the Vertac Chemical Company. It can be presumed that the waste burned during these tests had similar characteristics. Table 3 gives results of characterization analysis performed on a sample of the waste at the CRF. Table 4 summarizes the organic priority pollutant and EP toxicity trace metal concentrations in the waste.

2.3 SYSTEM OPERATION

2.3.1 Incinerator

The original test protocol document (1) specified performing six tests: a miniburn conducted at waste feedrate of 17 kg/hr (38 lb/hr), three runs with the stillbottoms waste fed at 34 kg/hr (75 lb/hr), and background runs with propane auxiliary fuel before and after the stillbottoms experiments. Due to unexpected difficulties, however, a 2-week period was spent developing an acceptable feed system. Consequently, the experimental program was scaled down to one background run, one miniburn, and two full-burn experiments. The background burn took place on September 4, 1985; the miniburn on September 9; the two full burn experiments took place on September 20 and 21.

Table 5 lists the nominal incinerator operating conditions for each of the tests performed. For all four, propane was fired in the kiln and the afterburner to maintain the kiln at about 1800°F and the afterburner at about 2000°F. This corresponded to heat inputs of about 260 to 350 kW (0.9 to 1.2 x 10^6 Btu/hr) in the kiln and about 470 to 560 kW (1.6 to 1.9 x 10^6 Btu/hr) in the afterburner for all four tests.

Combustion air was delivered to the burners by fans and the air flowrates were measured by pitot probes. These measurements were not sufficiently precise, however, because the air velocity was low and the pressure indicators were not ranged for the low-pressure signals. Hence these flowrates cannot be used to compute stoichiometries.

Two independent methods were used to estimate combustion product flowrates, namely helium tracer and Reference Method 5 duct flow determination. A description of the helium tracer apparatus and its operation is provided (2). The results of these two measurements are compared in Table 6. Theoretically, the combustion product flow should not change downstream of the afterburner. The measured increases in flowrate suggest that ambient air was still being drawn into the system, which was under negative pressure, downstream of the afterburner. The discrepancy between the helium tracer and Method 5 measured flowrates was in the 20 to

TABLE 2. APPROXIMATE WASTE GENERIC COMPOSITION BASED ON VERTAC DATA

Compound	Concentration (percent)
Methanol	1
Toluene	8
Dichlorobenzenes	1.5
Trichlorobenzenes	1.5
2,4,5-trichloroanisole	56
Na-trichlorophenol	7
Dichlorodimethoxybenzene	16
2,4,5-T, Na salt	7

TABLE 3. WASTE CHARACTERIZATION DATA

Bulk density, g/ml	1.37
Loss on drying, percent wt.	13.2
Ash, percent wt.	5.1
Heating value, MJ/kg (Btu/lb)	16.11 (6945)

TABLE 4. PRIORITY POLLUTANT COMPOSITION OF STILLBOTTOMS WASTE

Component	Concentration[a] (ppm, wt)	Detection limit (ppm, wt)
Volatile organic priority pollutants		
Methylene chloride	277	--
1,1-dichloroethylene	ND	42
1,1-dichloroethane	ND	42
t-1,2-dichloroethylene	ND	70
Chloroform	ND	84
1,2-dichloroethane	ND	42
1,1,1-trichloroethane	ND	42
Carbon tetrachloride	ND	70
Bromochloromethane	ND	42
1,2-dichloropropylene	ND	84
t-1,3-dichloropropylene	ND	42
Trichloroethylene	ND	42
Benzene	ND	110
1,1,2-trichloroethane	ND	42
Bromoform	ND	70
Tetrachloroethylene + tetrachloroethane	ND	84
Chlorobenzene	ND	42
Toluene	159,000	--
Semivolatile organic priority pollutants		
1,2-dichlorobenzene	2,690	--
1,2,4-trichlorobenzene	3,410	--
All other base/neutral semivolatile priority pollutants	ND	500
1,2-dichlorophenol	159	--
4-chloro-3-methylphenol	ND	500
2,4,6-trichlorophenol	ND	300
2,4-dinitrophenol	ND	300
4-nitrophenol	ND	500
2-methyl-4,6-dinitrophenol	ND	500
Pentachlorophenol	ND	500
All other acid semivolatile priority pollutants	ND	100

[a]ND denotes not detected at the detection limit noted.

TABLE 4. (concluded)

Component	Concentration[a] (ppm, wt)	Detection limit (ppm, wt)
Trace elements		
Antimony, Sb	ND	2
Arsenic, As	ND	1
Beryllium, Be	ND	3
Cadmium, Cd	ND	1
Chromium, Cr	ND	1
Copper, Cu	ND	1
Lead, Pb	4	1
Mercury, Hg	ND	1
Nickel, Ni	ND	1
Selenium, Se	ND	1
Silver, Ag	ND	1
Thallium, Tl	ND	1
Zinc, Zn	ND	10

[a]ND denotes not detected at the detection limit noted.

TABLE 5. INCINERATOR SYSTEM OPERATING CONDITIONS

	Background burn (9/4/85 0950 to 1940)		Miniburn (9/9/85 0945 to 1520)		First full burn (9/20/85 1030 to 2230)		Second full burn (9/21/85 1735 to 2330)	
	Range	Average	Range	Average	Range	Average	Range	Average
Kiln operation								
Propane heat input, kW (10^6 Btu/hr)	260 to 290 (0.9 to 1.0)	280 (0.95)	180 to 290 (0.6 to 1.0)	220 (0.72)	320 to 440 (1.1 to 1.5)	384 (1.3)	290 to 350 (1.0 to 1.2)	330 (1.1)
Waste feedrate, kg/hr (lb/hr)		0 0	8 to 23 (18 to 50)	17 (38)	0 to 25 (0 to 56)	10 (22)	2.7 to 40 (6 to 87)	18 (39)
Waste heat input, kW (10^6 Btu/hr)		0 0	37 to 101 (0.13 to 0.35)	77 (0.26)	0 to 114 (0 to 0.39)	44 (0.15)	12 to 180 (0.04 to 0.60)	80 (0.27)
Exit gas temperature, °C (°F)		950 (1750)		990 (1820)		980 (1800)		990 (1810)
Nominal residence time sec[a]		5.7		5.3		4.9		6.0
Afterburner operation								
Propane heat input, kW (10^6 Btu/hr)	470 to 500 (1.6 to 1.7)	480 (1.64)	440 to 500 (1.5 to 1.7)	470 (1.6)	500 to 590 (1.7 to 2.0)	560 (1.9)	500 to 560 (1.7 to 1.9)	520 (1.8)
Exit gas temperature, °C (°F)		1120 (2040)		1120 (2050)		1110 (2030)		1110 (2030)
Nominal residence time sec[a]		2.1		1.9		1.8		2.3
APCU operation								
System water makeup rate, L/min (gpm)	12 to 17 (3.2 to 4.4)	15 (4.0)	10 to 19 (2.7 to 4.9)	15 (3.9)	9.5 to 30 (2.5 to 7.8)	21 (5.5)	6.8 to 23 (1.8 to 6.0)	16 (4.3)
System blowdown rate, L/min (gpm)	6.8 to 9.1 (1.8 to 2.4)	8.2 (2.2)	4.9 to 8.3 (1.3 to 2.2)	7.2 1.9	3.4 to 13 (0.9 to 3.4)	8.7 (2.3)	4.5 to 11 (1.2 to 2.8)	8.7 (2.3)
Scrubber liquor pH	8.4 to 8.5	8.5	8.0 to 8.7	8.2	8.0 to 8.6	8.2	6.8 to 8.8	8.2
Venturi pressure drop, kPa (in. WC)	10.7 to 10.9 (43 to 44)	10.7 (43)	8.2 to 10.0 (33 to 40)	9.5 (38)	7.5 to 10.0 (30 to 40)	8.6 (35)	7.0 to 9.7 (28 to 39)	8.5 (34)
Venturi exit gas temperature, °C (°F)		79 (174)		80 (176)		81 (178)		82 (180)
Packed tower pressure drop, kPa (in. WC)	0.35 to 0.50 (1.4 to 2.0)	0.44 (1.8)	0.30 to 0.50 (1.2 to 2.0)	0.40 1.6	0.47 to 1.3 (1.9 to 5.2)	1.0 (4.1)	0.35 to 1.3 (1.4 to 5.4)	0.85 (3.4)
Packed tower exit gas temperature, °C (°F)		78 (172)		78 (173)		80 (176)		81 (178)

[a]Residence times based on volumetric flows calculated using the helium tracer system data.

TABLE 6. CALCULATED AVERAGE COMBUSTION GAS FLOWRATES (dscm/min)

Location	Background burn (9/4/85)		Miniburn (9/9/85)		First full burn (9/20/85)		Second full burn (9/21/85)	
	Velocity traverse[a]	Helium tracer[b]	Velocity traverse[a]	Helium tracer[b]	Velocity traverse[a]	Helium tracer[b]	Velocity traverse[a]	Helium tracer[b]
Kiln exit	c	7.0	c	7.5	c	8.2	c	6.7
Afterburner exit	c	12.9	c	13.7	c	15.1	c	11.5
E-duct	11.8	15.1	d	d	13.1	18.1	13.4	16.1
Stack	18.3	17.2	d	d	18.3	20.2	17.6	17.3

[a]From M5 trains.
[b]See (2).
[c]No velocity traverse performed at kiln or afterburner exits.
[d]No M5 trains run at E-duct or stack for miniburn.

30 percent range in the E-duct, and less than 10 percent at the stack. One possible explanation would be that the E-duct flue gas was not fully mixed, so that the helium concentration at the probe location was lower than the actual average concentration. This would result in helium tracer flowrate measurements being higher than those based on Method 5 velocity traverses. If this explanation were correct, then the stack gas was evidently better mixed since better agreement between helium tracer and velocity traverse measurements existed at this location.

The fact that Method 5 train sampling was not isokinetic (see Section 4) would not have an effect on the accuracy of a flue gas flowrate measurement based on a pitot tube velocity traverse.

The amount of waste fed into the kiln was monitored by recording the changes in the waste container weight reading. The feedrates fluctuated over a wide range, (see Section 4, Figures 13, 14, and 15), with mean rates of 17 kg/hr (38 lb/hr) on September 9, 10 kg/hr (22 lb/hr) on September 20, and at 18 kg/hr (39 lb/hr) on September 21, 1985. Waste characterization data were summarized in Section 2.2. With a measured heating value of 16.1 MJ/kg (6945 Btu/lb), the above feedrates corresponded to about 27 percent of the kiln heat input and 10 percent of the overall fuel input on September 9, 10 percent and 4.5 percent, respectively, for September 20, and 20 percent and 8.5 percent, respectively, for September 21, 1985, as reflected in Table 5.

During these tests, kiln and afterburner temperatures were controlled to about 980 and 1110°C (1800 and 2030°F), respectively, by adjusting the propane input rates. Indeed, this caused the propane heat input rates to vary. The combustion airflow methods were coupled with the propane flow control valve to maintain proper air-to-fuel ratios.

2.3.2 Air Pollution Control System

Two air pollution control subsystems were in operation during the tests. The operation of the "primary" subsystem, which included a venturi scrubber, wetted elbow, and a packed column scrubber, was monitored. In particular, the pH of the scrubbing liquor was maintained between 8.0 and 8.6 by addition of caustic (50-percent aqueous NaOH) solution to neutralize the HCl collected.

Individual flowrates of scrubber liquor into the venturi and the packed column scrubber were not monitored. Only the overall system water inlet (makeup) and discharge (blowdown) rates were monitored. These data were summarized in Table 5. Typically, 15 to 21 L/min (4.0 to 5.5 gpm) of makeup water enters the scrubber. Approximately 8.7 L/min (2.3 gpm) of scrubber liquor blowdown was discharged.

During the test period when the stillbottoms waste was fed into the kiln, this water was discharged to the onsite temporary blowdown storage tanks as noted in Section 2.1. During other times, it was discharged to the chemical sewer line which was processed by the waste water treatment plant at

the Pine Bluff Arsenal. Approximately 40 to 50 percent of the makeup water was evaporated and ended up as water vapor vented with the combustion gas products out the stack.

The pressure drop across the venturi scrubber was about 8.5 kPa (34 in. WC) with variations of about 1 kPa (4 in. WC). The packed column pressure drop ranged from 0.5 to 1.2 kPa (2 to 5 in. WC). The draft at the kiln ran at about -25 Pa (-0.1 in. WC) and hence would not leak any combustion gases. The large pressure drops across the venturi and the packed column scrubbers were supported by the large induced draft fan which pulled up to 11-kPa (45-in. WC) vacuum.

2.3.3 Residence Time Estimates

In addition to incineration temperature, residence time is an important parameter in the effectiveness of an incineration system in destroying hazardous organic compounds. For this test program, residence times were calculated based on volumetric flowrate measurements using the helium tracer system and the assumption that the kiln and afterburner chamber temperatures were isothermal and equal to the single point measurement, i.e., nominally 980°C (1800°F) at kiln and 1110°C (2030°F) at afterburner. It is recognized that the resultant residence times will not be precise, but they will serve as approximate indicators.

The calculated residence time in the kiln main chamber was 5.7 sec for the blank burn, 5.3 sec for the miniburn, and 4.9 and 6.0 sec for the two stillbottoms waste full burns. Residence times in the afterburner were 2.1, 1.9, 1.8, and 2.3 sec for the respective tests.

REFERENCES

1. "Protocol for an Incineration Study of 2,4,5-T Stillbottoms with TCDD Contamination," prepared by Versar, Inc., Southern Operations, for EPA/HWERL, Combustion Research Facility, July 1985.

2. Carnes, R. A., and F. C. Whitmore, "Characterization of the Rotary Kiln Incinerator System at the USEPA Combustion Research Facility (CRF)," Hazardous Waste, Vol. 1, No. 2, p. 225 (1984).

SECTION 3

SAMPLING AND ANALYSIS PROTOCOL

The incinerator flue gas and residual stream sampling procedures used and the analysis protocols employed to determine the composition of samples collected is summarized in this section. The sampling procedures employed are discussed in Section 3.1; Section 3.2 outlines the analytical protocols used.

3.1 SAMPLING PROCEDURES

The combustion gas generated during each test was monitored at various locations in the system for CO, CO_2 O_2, NO_x, total hydrocarbon (THC), HCl, particulate and trace semivolatile organic compounds, most importantly 2,3,7,8-TCDD. The methodologies for these efforts are discussed in Section 3.1.1 and 3.1.2 below. In addition, grab samples were obtained of the waste feed, the scrubber system blowdown liquid, and the ash collected in the ash pit during the tests. Procedures for obtaining these samples are briefly outlined in Section 3.1.2.

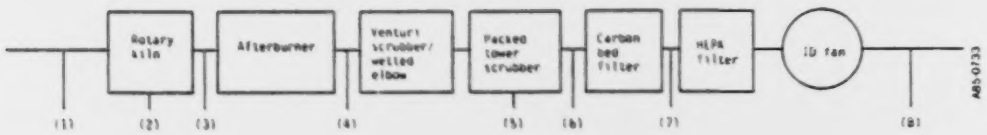
Ambient air sampling, both in the high bay incinerator room and in the outside vicinity of the CRF was also performed. Procedures and results of these efforts are described in Section 7. Figure 2 summarizes the sampling locations and types of samples obtained for this series of experiments.

3.1.1 Continuous Emission Monitoring

Online instrumentation was used for monitoring CO, CO_2, O_2, NO_x, and THC. Table 7 lists the instruments used to monitor each of these and their principle of operation.

Combustion gas can be monitored on a time-sharing basis at the kiln transfer duct and at the afterburner exit. However, for these tests, all data were taken at the afterburner exit. The monitoring system serving these two locations is shown schematically in Figure 3. This system consists of:

- 66-cm (26-in.) Hastelloy C-276 probes
- 12m (40 ft) of 1/4-in. heat-traced Teflon line
- Liquid water bubbler for moisture and particulate removal
- Air actuated valves that select the desired sampling location
- 12m (40 ft) of 1/4-in. polyethylene transfer line



Parameter	Test points	Methodology	Sample duration	No. of samples
CO_2	3,4,8	NDIR	Continuous	--
O_2	3,4,8	Zirconium oxide sensor	Continuous	--
CO	3,4,8	NDIR	Continuous	--
NO_x	3,4,8	Chemilluminescence	Continuous	--
HCl	6	Colorimetric	Continuous	--
THC	6,7	Flame ionization detector	Continuous[a]	--
Semivolatile organics including 2,3,7,8-TCDD	3,4,6,8	Modified Method 5	10 hours (7 dscm (250 dscf))	2 at test pt 3 2 at test pt 4 4 at test pt 6 2 at test pt 8
Waste	1	Grab		3
Kiln ash	2	Grab	8 composites after entire burn series	8
Scrubber blowdown	5	Grab	8 composites after entire burn series	8

[a]The two test points were monitored by one instrument on a 5-min. time-sharing basis.

Figure 2. Summary of the general sampling protocol.

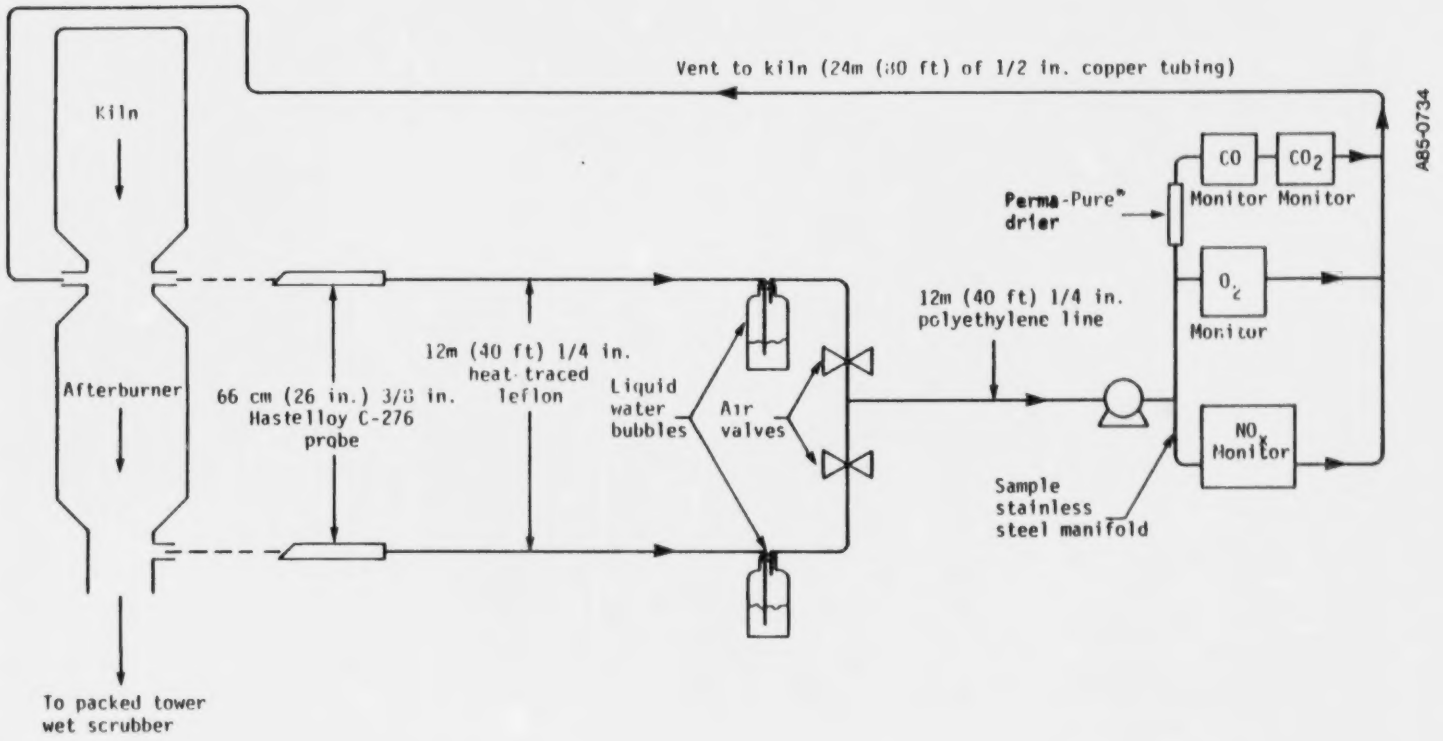


Figure 3. Schematic of the continuous emissions monitoring system for kiln and afterburner.

TABLE 7. CONTINUOUS EMISSIONS MONITORS AVAILABLE AT THE CRF

Parameter	Instrument manufacturer and model no.	Method of detection	Range
O_2	Bendix Model 304	Zirconium oxide	0 to 25 percent
CO	Bendix Model 8903	NDIR	0 to 100 ppm 0 to 1000 ppm
CO_2	Bendix Model 8903	NDIR	0 to 10 percent
NO_x	Bendix Model 8101C	Chemiluminescence	0 to 150 ppm
THC	Beckman Model 402	Flame ionization	0 to 50 ppm

- A Perma-pure® drier, for additional moisture removal (conditions CO/CO_2 sample stream only)
- Sample pump and stainless-steel manifold delivery system
- Analyzers for CO, CO_2, O_2, and NO_x

Each of these instruments vents the sample back to the kiln via a 1/2-in. copper line.

The combustion gas leaving the stack can also be monitored on a time-shared basis using the same bank of monitors noted above. The stack gas sampling system is illustrated in Figure 4 and consists of:

- 61-cm (24-in.) 3/8-in. stainless-steel probe
- 91-cm (36 in.) of 1/4-in. polyethylene transfer line
- Water droplet removal vessel
- 15m (50 ft) of 1/4-in. heat-traced Teflon transfer line
- Liquid water bubbler for additional water removal
- 12m (40 ft) of 1/4-in. polyethylene transfer line
- Further gas conditioning and analyzers as noted above

A separate continuous monitoring system shown schematically in Figure 5 uses a THC analyzer to provide information on the efficiency of the carbon-bed absorber. This system alternately measures the THC concentration in the combustion gas entering the bed and leaving the bed. Each of these two sample points is served by:

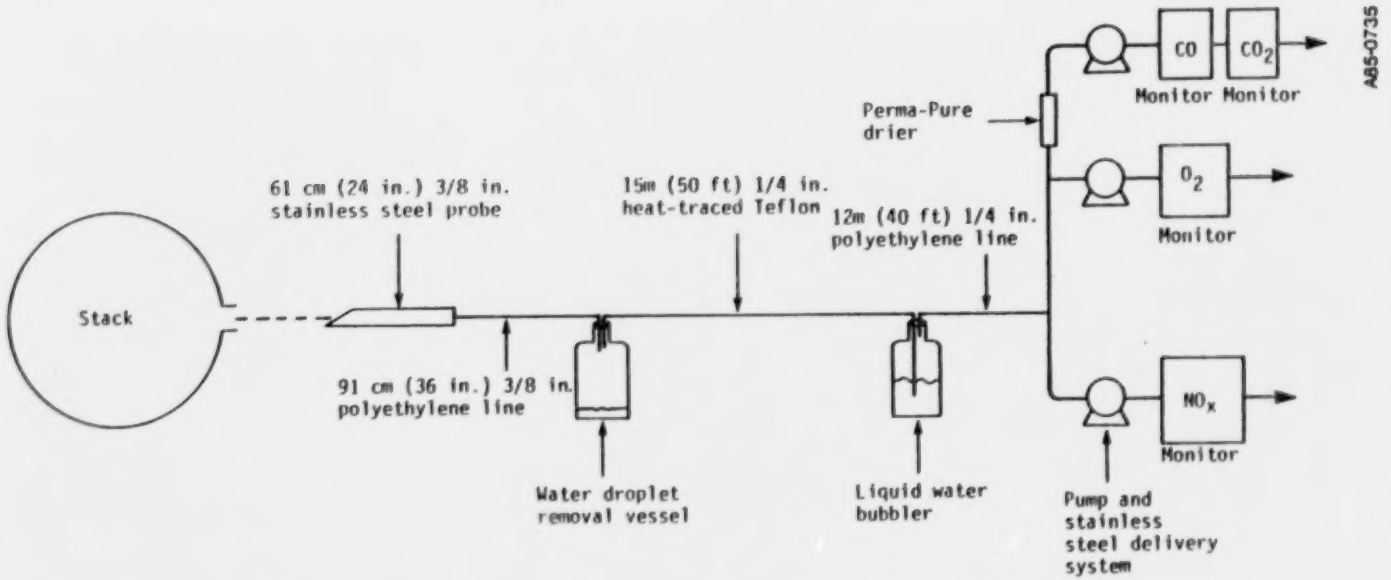


Figure 4. Schematic of the continuous emissions monitoring system for the stack.

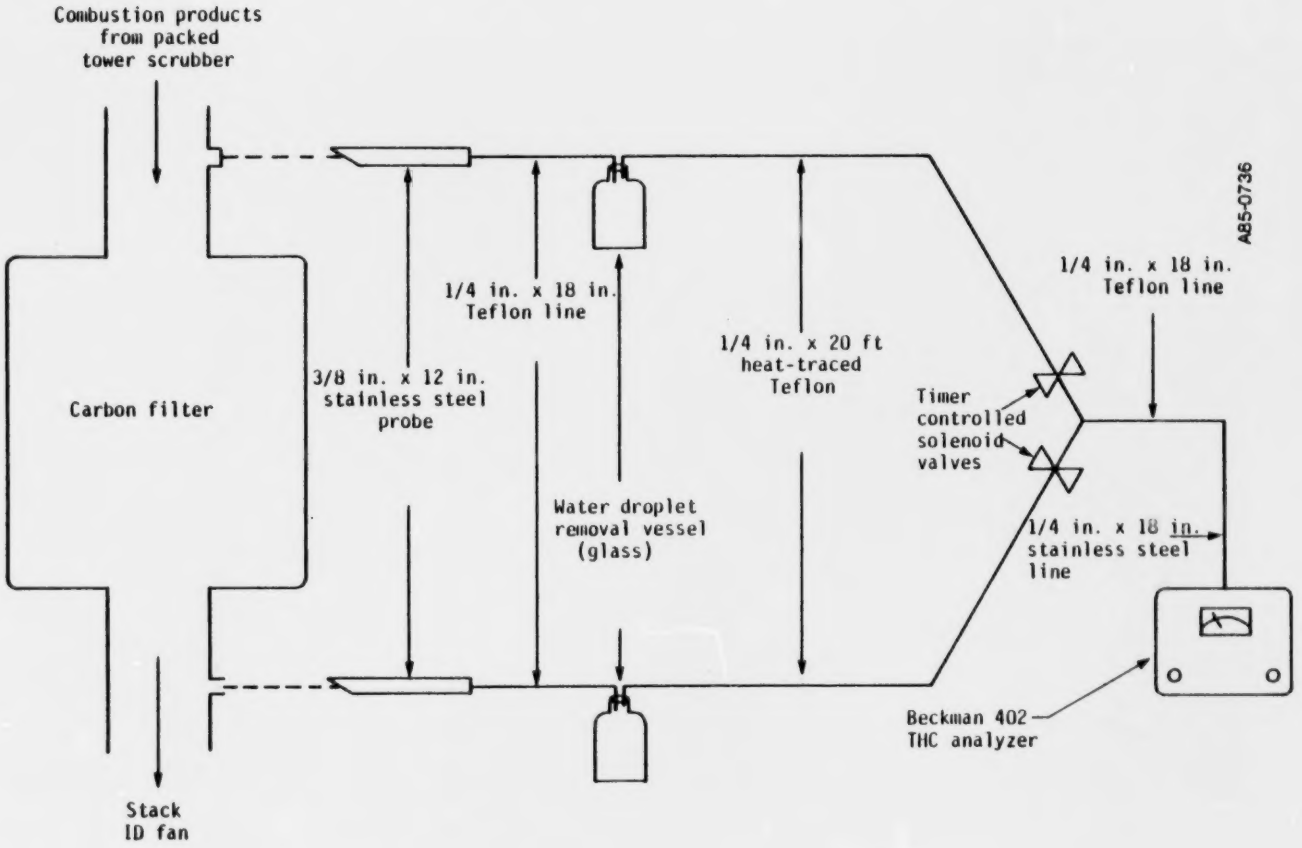


Figure 5. THC monitoring system schematic.

- 30-cm (12-in.) 3/8-in. stainless-steel probe
- 46-cm (18-in.) of 1/4-in. Teflon transfer line
- Glass water droplet removal vessel
- 6m (20 ft) of 1/4-in. heat-traced Teflon line
- A timer-controlled solenoid valve (5-min. cycle)

The two sample lines converge to 46-cm (18-in.) of 1/4-in. Teflon transfer line. This in turn is converted to 46-cm (18-in.) of 1/4-in. stainless-steel transfer line that enters the Beckman 402 THC analyzer.

3.1.2 Continuous HCl Monitoring

In addition to the traditional combustion gas continuous analyzer system described above, HCl emissions were continuously measured in the flue gas at the E-duct location during the miniburn test on September 9 and the full burn test on September 20. These measurements were performed using a CEA model TGM 555 colorimetric analyzer placed at the E-duct location.

The TGM 555 monitor is an automated wet-chemical colorimetric analyzer. In principle, hydrogen chloride liberates thiocyanate ion in mercuric thiocyanate solution by the formation of soluble mercuric chloride. In the presence of ferric ion, highly colored ferric thiocyanate is produced. The intensity of the color formed is measured at 480 nm and is proportional to the concentration of hydrogen chloride present. The instrument has a digital meter that reads out as a percent of full scale, and is capable of exceeding 100 percent. For example, if the unit is calibrated for 0-2 ppm full scale for a chemistry that is linear up to 3 ppm, a reading of 063 on the meter would indicate 1.26 ppm, and 112 would be 2.24 ppm.

The TGM 555 measured the concentration of hydrogen chloride in the E-duct gas by monitoring the amount of color change produced in the analyzer's working color reagent system. Flue gas was continuously drawn into the instrument via an internal vacuum pump through an appropriate Teflon fitting, and then through a vertical glass gas/liquid contact absorber coil. Reagent absorbing solution was drawn from its reservoir by the liquid pump and was transported concurrently downward with the air stream through the coil to absorb the gas parameter to be measured. The absorbing solution reacts with the effluent and produces a color change. Unreacted reagent is pumped through the reference cell of the dual-beam colorimeter of the TGM 555. The colored reaction product flows through the sample cell. The colorimeter measures electronically the difference in light absorption of the reagent before and after the reaction with the hydrogen chloride. Transmission of light through the flow cell is measured by a matched set of photodetectors at a particular wavelength.

The electrical signal generated in the colorimeter is amplified and fed to a digital display where it is read out as a percentage of full scale. The measurement range of the instrument can be adjusted to be 0 to 1.0 ppm to 0 to 50 ppm or even higher with the addition of a sample splitter.

3.1.3 Semivolatile Organic Compound Measurement

Semivolatile organic compound emissions, most importantly 2,3,7,8-TCDD, the POHC for these tests, were measured at four locations in the system as shown in Figure 2. The sampling methodology followed that outlined in the ASME MM5 protocol (3) with some modifications necessitated by the conditions presented by the environments of the different sampling locations.

Sampling conducted at the kiln transfer duct and afterburner exit duct utilized a combination condenser/resin capsule unit. Conditions at these locations were unsuitable for isokinetic sampling so strict MM5 procedures and equipment were not employed. The sampling train shown in Figure 6 was used to sample at this location. This train consisted of:

- 61-cm (24-in.) 1/4-in. Hastelloy C-276 probe
- An unheated 46-cm (18-in.) 1/4-in. Hastelloy C-276 transfer line
- Inline, type-J thermocouple
- An unheated 15-cm (6-in.) 3/8-in. Teflon transfer line
- Glass fiber filter assembly
- Condenser/resin capsule assembly containing 30g of XAD-2 resin
- A second type-J thermocouple
- Empty Smith-Greenberg impinger
- Smith-Greenberg impinger containing 750g of silica gel

In assembling the train, Teflon sleeves, rather than grease, were used in the joints located upstream of the XAD-2 resin.

Though no additional heat was added to the transfer line and filter assembly, the temperature of the sample gas measured just ahead of the filter was usually 95° to 120°C (200° to 250°F) during sampling, in the range specified in Reference to Method 5.

At the beginning of each sampling period, flowrates through the resin averaged 20 to 25 L/min. During the course of a 10-hour sampling period, however, increased particulate loading on the filter would typically cause a reduced flow to the 5- to 10-L/min range.

For each test performed (blank burn, miniburn, and two full burns) two sampling trains were run simultaneously at both the kiln transfer duct and the afterburner exit. Plans for each test were to operate all trains for a 10-hour period during which nominally 7 dscm (250 dscf) of combustion gas would have been collected. However, during most tests, operational problems often developed which resulted in the collection of smaller volumes at some locations.

When sampling was complete, the train was leak tested, disconnected from the probe/transfer line assembly, and transported to the laboratory for sample recovery. The probe and transfer line were sealed at each end and transported to the laboratory where they were rinsed three times with 500 ml

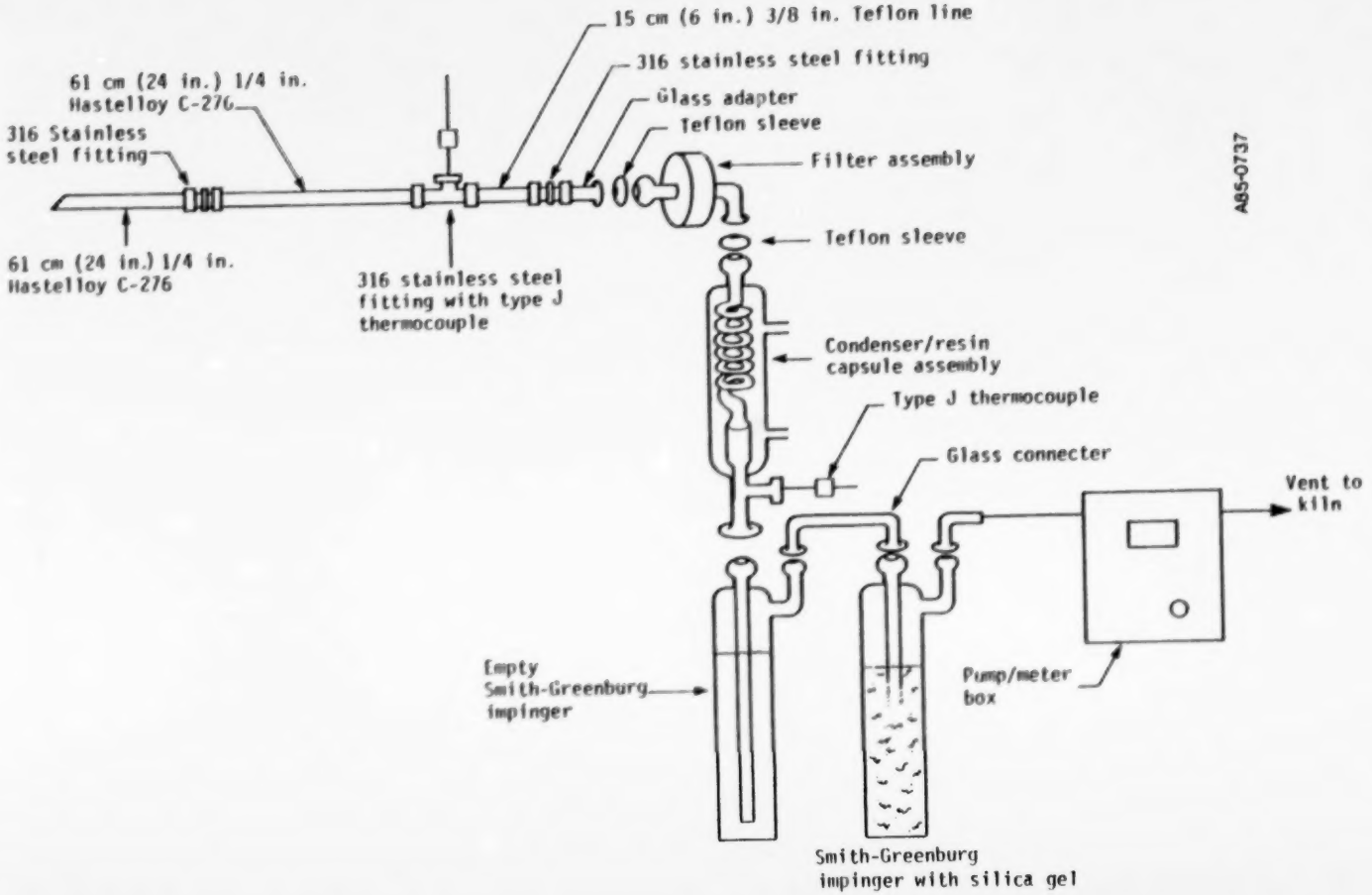


Figure 6. Hot zone sampling system.

of a 1:1 mixture of methanol and methylene chloride. Probe rinses became another sample for analysis.

Sampling for semivolatile organics also took place in the horizontal duct between the packed tower scrubber and the carbon-bed absorber, referred to herein as the E-duct. The carbon bed allows for operation of the incinerator under experimental, noncompliance conditions by providing purification of flue gas before it is emitted to the atmosphere. For these incineration experiments, the E-duct was the sample point of choice because it is at this point that the CRF's flue gas mimics a typical incinerator's stack emissions.

The sampling system used consisted of four identical trains, each connected to its own fixed probe/pitot tube assembly. The train/probe assemblies are described in detail in the following and illustrated in Figure 7.

- Probe/pitot tube assembly: A 1/2-in. OD 316 stainless probe nozzle was connected to a 3/8-in. OD glass probe with a 5/8-in. to 3/8-in. 316 stainless-steel reducing union tube fitting and Teflon ferrules. The glass probe was sheathed with a 1/2-in. OD stainless-steel tube which was butt welded to the nut of the 3/8-in. side of the reducing union (as is done with most commercially available sampling probes). A second 3/8-in. nut was welded to the other end of the 3/8-in. probe sheath and Teflon ferrules were used to seal this end of the glass probe to the sample line. A type "S" pitot tube was mounted along the side of the above-mentioned probed sheath, as required by Method 2. The entire assembly was sheathed by a 1-in. OD 3/8-in. stainless-steel tube which was sealed in the duct port with a tube fitting and teflon ferrule. To prevent ambient air from leaking into the duct through the sheath, a sealant was placed inside the sheath in a 6-in. plug that was located 7.5 to 10 cm (3 to 4 in.) back from that end of the sheath which is exposed to the stack gas.

- Sample line: A 61-cm (24-in.) length of 3/8-in. OD Teflon line was attached to the probe assembly with a 316 stainless-steel tube fitting

- Condenser/resin cartridge assembly: The Teflon sample line was connected to a 28/15 glass socket with a 316 stainless-steel tube fitting and teflon ferrules. This socket was sealed to the inlet of the condenser/resin cartridge assembly, with the use of a Teflon sleeve. All glass to glass joints located upstream of the resin capsule were sealed with the use of Teflon sleeves, rather than grease.

- Moisture removal components: The outlet of the assembly sat on top of a 4L condensate trap, connected to an impinger containing silica gel via a glass elbow

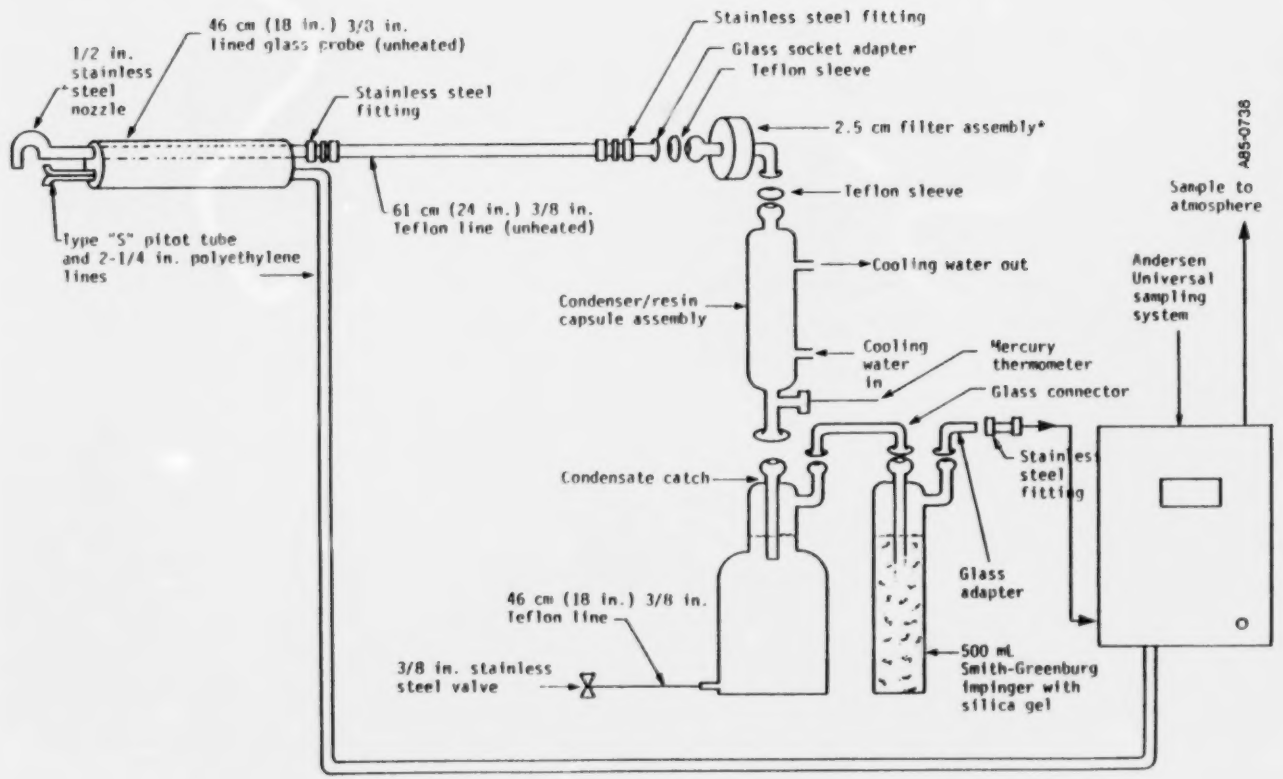


Figure 7. E-duct sampling system.

This train was used for the blank burn conducted on September 4, during which no waste was introduced to the incinerator. During the waste feed full burn on September 20 a heated filter was added to the train. The 61-cm (24-in.) 3/8-in. Teflon line was connected to the inlet of the heated filter with the use of a glass socket adapter and a stainless-steel tube fitting. The outlet of the filter connected to the condenser/resin cartridge assembly in the same manner. During the September 21 full burn, an unheated filter was used, plumbed in the train as described above.

As was noted above the "8 and 2 diameter" requirement of Method 2 necessitates an inordinate length of duct if four simultaneous samplers are to be used at four separate sampling locations. However, a valid isokinetic sample can be obtained if the four samplers are served by separate probes, each sampling in the same vertical plane at one-half the required number of points on the two perpendicular traverse lines. Because all probes sampled from the same vertical plane, only a 3.7-m (12-ft) length of duct was required. Figure 8 shows a cross section of the E-duct, along with the location of the four probes.

For a 35-cm (14-in.) diameter duct, Method 1 requires four points on each perpendicular traverse line. When sampling began, each of the probes were positioned at the outer-most points of the two traverse lines. With the probes in this position, flue gas was sampled at half of the required eight traverse points. Later in the experiment, each of the four probes were simultaneously moved inward to the next traverse point. Thus the duct was being sampled at the remaining four points. Because all four pitot/probe assemblies were located in the same vertical plane, they did not affect each other. A thermocouple probe was used to measure the stack gas temperature at four points on a horizontal traverse line located 61 cm (2 ft) upstream of the sample point.

To detect leaks, which may have resulted from moving the probes, helium tracer was injected into the incinerator system for the duration of the experiment. After the probes were moved and re-sealed in the duct ports, Mylar gas sample bags were connected to each of the sampler's pump exhaust. Simultaneously, a 5-L/min sample of flue gas was extracted from the duct and conveyed to a thermal conductivity gas chromatograph. By comparing the peak height of this sample to that generated by a manual injection of sample from the Mylar bag, any ambient air leak into the duct was evident.

At the conclusion of each experiment, the sample trains were disconnected from the transfer lines, and the probe, transfer lines, filters, and trains were sealed and transferred to the laboratory where all train components located upstream from the resin were rinsed as described earlier. The filter and resin were extracted and these extracts, along with the above-mentioned rinses were cleaned and reduced to 1 ml. Thus reduced, the extracts of all four samples were analyzed by GC/MS to quantitate the DRE for 2,3,7,8-TCDD.

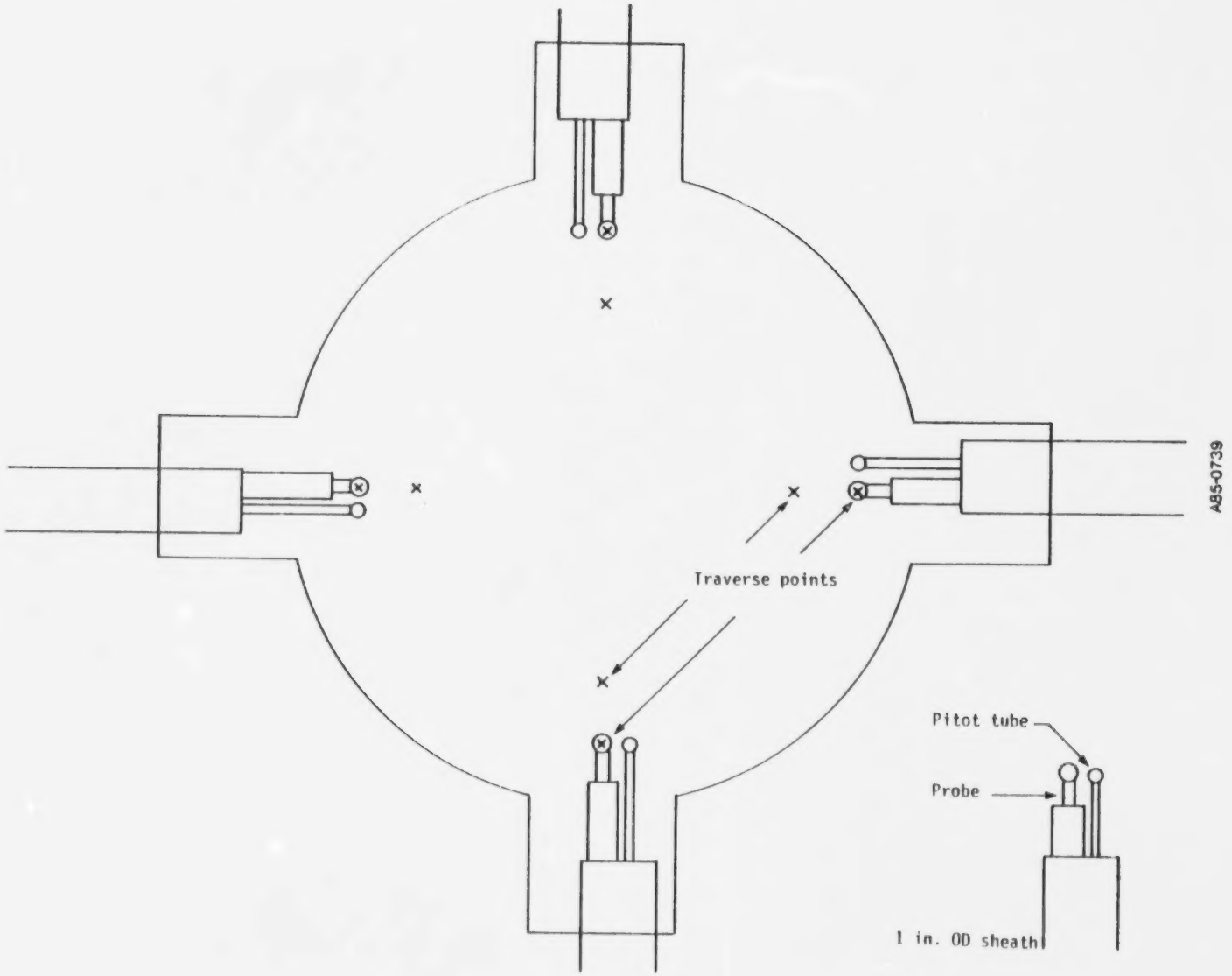


Figure 8. E-duct probe orientation.

Trace organics were measured in the stack emissions with the use of two standard MM5 trains as shown in Figure 9; each of these consisted of:

- Stainless-steel probe nozzle
- Glass-lined probe/pitot tube assembly
- Heated filter
- 3/8-in. OD Teflon transfer line (unheated) which connected to the filter with a 28/15 glass socket. The socket was connected to the Teflon line with a 3/8-in. stainless-steel tube fitting.
- Condenser/resin cartridge assembly, which was connected to the Teflon transfer line with a 28/15 socket and tube fitting as described above. At the outlet of the resin cartridge, a liquid-in-glass thermometer was sealed in the assembly with a threaded adapter. This provided temperature measurement of the cooled sample.
- The condenser/resin capsule assembly connects directly to a 4L condensate catch, with the use of a 28/15 ball/socket combination
- Smith-Greenburg impinger, containing silica gel. This impinger connected to the condensate trap with the standard 28/15 ball socket "U" connector.

As was noted in the discussion of the other sample trains, Teflon sleeves, rather than grease, were used in those joints located upstream from the resin capsule.

The two trains were operated simultaneously in the stack downstream of the indirect draft fan, each train traversing only one of the traverse lines in a manner such that one probe did not interfere with the other. This was accomplished by starting the sample with the probe of one train positioned at the traverse point furthest from the duct port, while the other probe started its traverse at the point closest to the duct port as illustrated in Figure 10. The particulate collected in the front half of each train was combined to determine the particulate emission rate. The resin from each sampler was extracted and these extracts combined and analyzed by GC/MS to determine 2,3,7,8-TCDD levels in the stack emissions.

3.2 ANALYSIS PROTOCOL

Table 8 summarizes the total number of samples obtained during each of the tests performed in this program. A total of 80 samples was obtained; 70 were analyzed and 10 archived. There are seven different sample types represented in this enumeration.

A variety of anaytical procedures was used to determine parameters of interest in samples selected from Table 8. For example, ambient air, kiln

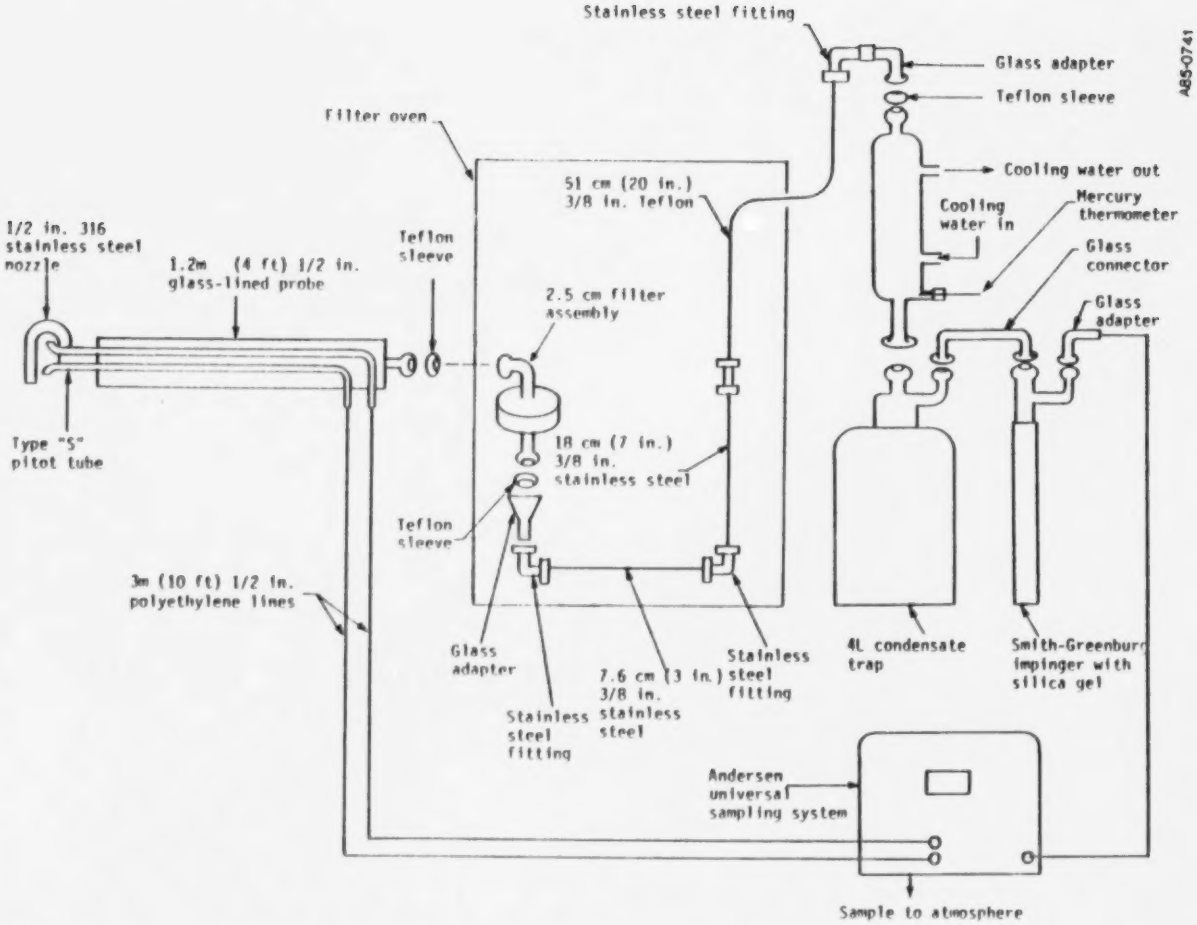


Figure 9. Stack sampling system.

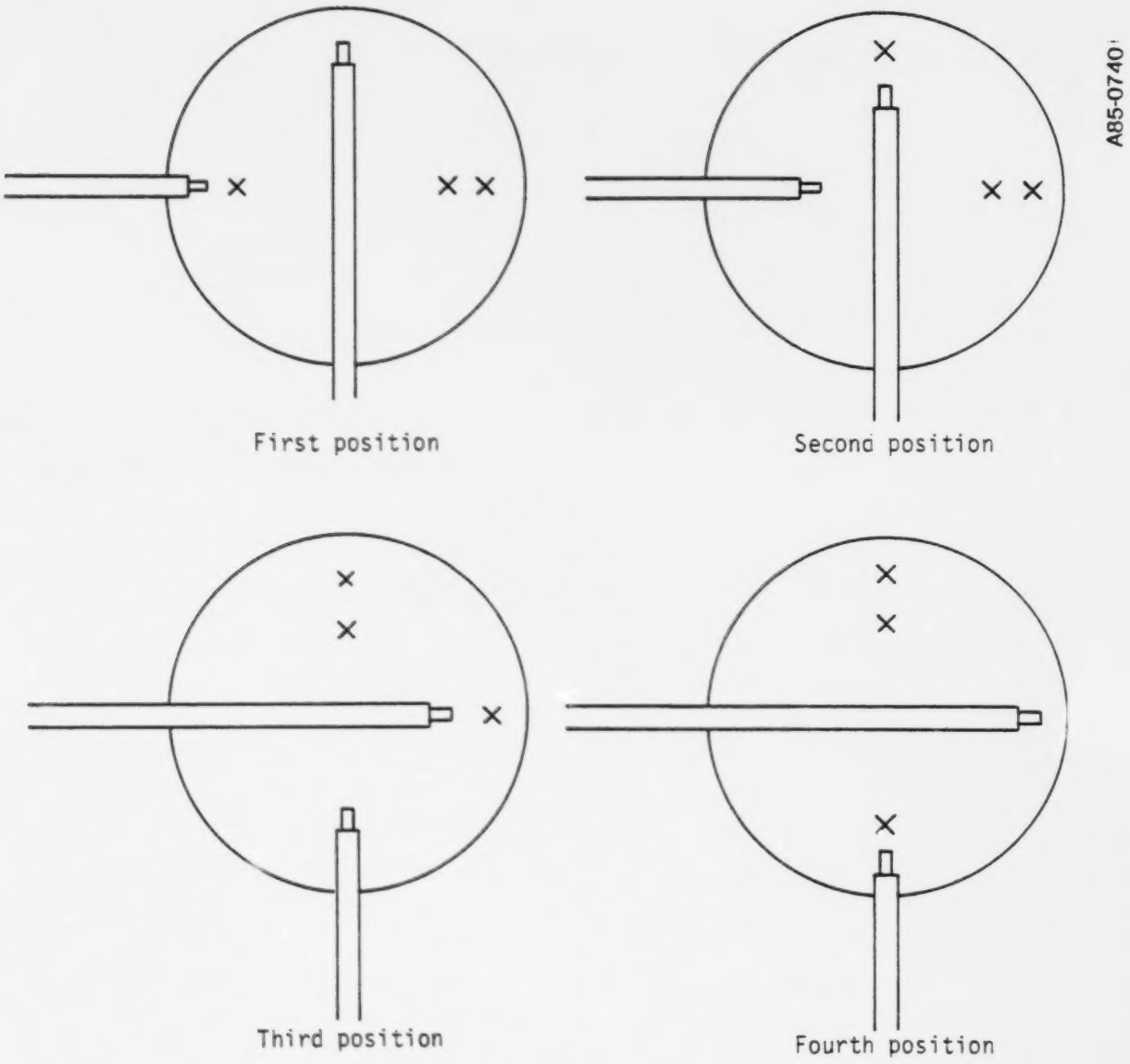


Figure 10. Simultaneous dual-probe traverse employed at the stack location.

TABLE 8. SAMPLES OBTAINED DURING VERTAC WASTE TEST BURNS

Sample type	Sample dates					Sample total
	9/4/85	9/9/85	9/20/85	9/21/85	Other	
Waste samples:						
• Preburn samples					6	6
• Incinerator feed samples					2	2
MM5 incinerator samples:						
• Kiln transfer duct	2	2	2	2		8
• Afterburner duct	2	2	2	2		8
• E-duct	4		4	4		12
• Stack	2		2	2		6
Scrubber blowdown samples					8	8
Air samples (see Section 7)	1		6		2	9
HCl samples:						
• Continuous analyzer (CEA)		1	1			2
• MM5 impingers		1	4			5
Kiln bottom ash					8	8
Q.C. samples:						
• Field spike (MM5)	1		1	1		3
• Field blank (MM5)	1		1	1		3
					Total	80

bottom ash, and scrubber blowdown liquid were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) for polychlorinated dibenzofurans (PCDF) and polychlorinated dibenzo-p-dioxins (PCDD) of chlorine substitution 4 through 8. Flue gas samples were analyzed by HRGC/HRMS for 2,3,7,8-TCDD only. Waste samples were analyzed by bomb calorimetry for higher heating value. The analytical methodologies used are summarized in detail in the following subsections.

3.2.1. Extraction and Analysis of Ash and Air Samples

Each of these samples was spiked with isotopically labeled internal standards and Soxhlet extracted for approximately 18 hours using benzene. The ash samples were spiked with 25 ng each of 2,3,7,8-tetrachlorodibenzo-p-dioxin-$^{13}C_{12}$ (2,3,7,8-TCDD-$^{13}C_{12}$), 2,3,7,8-tetrachlorodibenzofuran-$^{13}C_{12}$ (2,3,7,8-TCDF-$^{13}C_{12}$), and octachlorodibenzo-p-dioxin-$^{13}C_{12}$ (OCDD-$^{13}C_{12}$), while the air samples, which had been spiked with 2.5 ng each of 2,3,7,8-TCDD-$^{13}C_{12}$ and 2,3,7,8-TCDF-$^{13}C_{12}$ before sampling, were spiked only with 5 ng of OCDD-$^{13}C_{12}$.

The benzene extracts were concentrated to approximately 4 ml using three-stage Snyder columns, and transferred to multilayered columns containing activated silica gel, 44-percent concentrated sulfuric acid on silica gel, and 33-percent 1M sodium hydroxide on silica gel. The columns were rinsed with 70 ml of hexane and the entire elutates were collected. The purpose of these columns was to remove acidic and basic compounds from the extracts as well as oxidizable materials.

The benzene/hexane elutates were concentrated using a gentle stream of nitrogen gas and solvent exchanged into hexane. The hexane solutions were chromatographed through columns containing approximately 1 gm of activated basic alumina using methylene chloride (97:3, v/v), and hexane/methylene chloride elutates were collected, concentrated to near dryness, and dissolved in 20 µl of an absolute recovery standard containing 1,2,3,4-TCDD-$^{13}C_{12}$. All solutions were stored at 0°C and protected from light until analyzed.

The extracts were analyzed for PCDD/PCDF using capillary column HRGC/HRMS. The HRGC/HRMS consisted of a Carlo Erba Model 4160 GC with Model 7070 mass spectrometer. The primary chromatographic column was a 30-m DB-5 fused silica column using helium carrier gas at a flow velocity of 25 cm/sec. The mass spectrometer was operated in the electron impact (EI) ionization mode at a mass resolution of 9,000 to 12,000 (M/ΔM, 10-percent valley definition). The operating parameters of the HRGC/HRMS are summarized in Table 9. The primary analyses, to determine the total level of each PCDD/PCDF class, were carried out using two separate HRGC/HRMS runs. This was necessary due to chromatographic overlap of adjacent isomer classes and hardware limitations to the number of masses that could be sequentially monitored. The first run provided data for the PCDD and PCDF isomers having an odd number of chlorine substituents, while the second run determined the levels of the isomers containing an even number of chlorines. Although the DB-5 capillary column is excellent for PCDD/PCDF isomer class determinations, it does not provide the isomer specificity of the more polar phase columns.

TABLE 9. HRGC/HRMS OPERATING PARAMETERS

Mass resolution	9,000 to 12,000 (M/ΔM, 10-percent valley definiton)
Electron energy	70 eV
Accelerating voltage	6,000 volts
Source temperature	200°C
Preamplifier gain	10^7 volts/amp
Electron multiplier gain	~10^6
Transfer line temperature	280°C
Column	DB-5 30m or CP Sil-88 50m
Injector temperature	300°C
Column temperature -- initial (3 min)	160°C
Column temperature -- program	30°C/min
Column temperature -- final	250°C (CP Sil-88)
	290°C (DB-5)
Carrier gas	Helium
Flow velocity	~25 cm/sec
Injection mode	Splitless
Injection volume	2 µl

Since 2,3,7,8-TCDD and 2,3,7,8-TCDF are the most toxic PCDD/PCDF isomers, all samples that were found to contain TCDD or TCDF using the DB-5 column were reanalyzed using a 50-m CP Sil-88 fused silica capillary column which resolves 2,3,7,8-TCDD from the other 21 TCDD isomers. While this column does not provide complete separation of 2,3,7,8-TCDF from the other 37 TCDF isomers, the level of confidence is far greater than with the DB-5 column and is considered to be state of the art. All HRGC/HRMS data were acquired by multiple-ion-detection using a VG Model 2035 Data System. The exact masses that were monitored are shown in Table 10.

3.2.2 Extraction and Analyses of Water Samples

Each water sample was filtered. The liquid portion of each sample was spiked with 5 ng of 2,3,7,8-TCDD-$^{37}Cl_4$ and 20 ng of hepta-CDD-$^{37}Cl_7$ and extracted with methylene chloride. The solid particulate matter samples were spiked with 5 ng of 2,3,7,8-TCDD-$^{13}C_{12}$, 2 ng of hexa-CDD-$^{13}C_{12}$, and 20 ng of octa-CDD-$^{13}C_{12}$ and Soxhlet extracted with benzene for 16 hours.

Extracts of the liquid and particulate samples were subjected to separate cleanup procedures using micro alumina and carbon columns. Aliquots of each of the two extracts representing an original water sample were coinjected into a 30m SE-54 fused silica capillary column for HRGC/HRMS analysis.

Similar extracts were also analyzed for the semivolatile organic priority pollutants by Method 8270.

Whole water samples were analyzed for the halogenated volatile organic priority pollutants by purge and trap GC/electron capture detector (ECD) by Method 8010.

3.2.3 Extraction and Analysis of MM5 Incinerator and QC Samples

Sample harvesting and processing from MM5 trains were performed in the CRF laboratory by the chief chemist, his assistant and two technicians. Several practices were adopted to minimize cross-contamination among trains. These included:

- All samples from one burn must have cleared the laboratory before another burn can be initiated
- All the glassware used to assemble a train, and to process the sample extract harvested from it, constituted a unique set and were always used together to take and harvest samples from the same incinerator location
- A given train was processed from receipt in the laboratory to finished extract by one and only one worker

Each MM5 sample consisted of impinger condensate, probe washes, glass fiber filter catch, and XAD-2 sorbent resin.

TABLE 10. EXACT MASSES USED FOR THE DETERMINATION OF PCDD AND PCDF

Compounds	Accurate mass		Theoretical isotope ratio
	Mass 1	Mass 2	Mass 1/Mass 2
Tetrachlorodibenzo-p-dioxins	319.8965	321.8936	0.77
Tetrachlorodibenzofurans	303.9016	305.8987	0.77
Hexachlorodiphenyl ethers	375.8364	377.8334	1.23
Pentachlorodibenzo-p-dioxins	355.8546	357.8517	1.54
Pentachlorodibenzofurans	339.8597	341.8567	1.54
Heptachlorodiphenyl ethers	409.7975	411.7944	1.03
Hexachlorodibenzo-p-dioxins	389.8156	391.8127	1.23
Hexachlorodibenzofurans	373.8207	375.8178	1.23
Octachlorodiphenyl ethers	433.7584	445.7555	0.88
Heptachlorodibenzo-p-dioxins	423.7766	425.7737	1.03
Heptachlorodibenzofurans	407.7817	409.7737	1.03
Nonachlorodiphenyl ethers	477.7194	479.7165	0.77
Octachlorodibenzo-p-dioxin	457.7377	459.7347	0.88
Octachlorodibenzofuran	441.7428	443.7398	0.88
Decachlorodiphenyl ethers	551.6805	513.6775	0.69

Each impinger condensate was spiked with 25 ng of 2,3,7,8-TCDD-$^{13}C_{12}$ and 5 ng of 2,3,7,8-TCDD-$^{37}Cl_4$ and extracted using three 60-ml aliquots of methylene chloride in a separatory funnel. The methylene chloride extracts were concentrated using Kuderna-Danish (K-D) concentrators to 10 ml and quantitatively transferred to the Soxhlet thimble.

The probe, connecting tube, and front half of the filter holder were first brushed and then washed (6 x 30 ml) with methylene chloride/methanol (1:1). The brushing and washings were reduced to less than 5 ml in a K-D and quantitatively transferred to the Soxhlet thimble in the following step using <2-ml methanol and <20-ml benzene.

The glass fiber filter and XAD-2 were tranferred to a Soxhlet thimble that already contained a bed of precleaned silica gel. The back half of the filter holder, frit, connecting tube, and sorbent module were rinsed with benzene through the thimble and into the extractor.

The XAD-2 absorbent was spiked with 25 ng of 2,3,7,8-TCDD-$^{13}C_{12}$ and 5 ng of 2,3,7,8-TCDD-$^{37}Cl_4$. Audit/XAD-2 samples (spike and recovery) were also prepared to correspond to the test performed on September 4, 20, and 21. The September 4 audit resin sample was spiked with 20 ng of native 2,3,7,8-TCDD in addition to the labeled surrogates noted above, while the audit resin samples of September 20 and 21 were each spiked with 200 ng of this material. Each resin sample was Soxhlet extracted for 8 hours with benzene. The extract volume was reduced to <12 ml in the same Kuderna-Danish concentrator used for probe washes and impinger samples for a given train. Further concentration to 20 ml was accomplished by gentle dry nitrogen blowdown. The extracts were split; 9.0 ml were sent to a dioxin-certified outside laboratory for 2,3,7,8-TCDD determination and 1.0 ml remained at the CRF.

A 5.0-ml aliquot of each 9.0-ml extract was cleaned up prior to HRGC/LRMS analysis using methods found in the EPA dioxin analysis documents designated by IFB WA 84-A002, subsequently referred to as the EPA-CLP analytical methods. These standard extract cleanup procedures include multilayer acid/base silica gel and basic alumina gravity column chromatrography with PX-21 carbon/celite 545 and silica/diol column techniques reserved for demanding samples.

The samples from the September 4 burn were unique only in that their extract volumes were reduced to 1.0 ml at the CRF; 0.9 ml was sent out for analysis, which was performed on a 0.5-ml aliquot; and 0.1 ml was retained at the CRF as an archive. All other preparative and analytical procedures employed for these train extracts were identical with those described above and in the following paragraphs.

The samples were analyzed by GC/MS following the EPA-CLP analytical methods summarized as follows:

- With a stream of dry, filtered nitrogen, reduce the extract volume to near dryness. Immediately before GC/MS analysis, adjust the extract volume to 50 µl with toluene.

- Inject a 2-µl aliquot of the extract into the GC, operated under acceptable calibration procedures to produce acceptable results with the performance check solution

- Acquire mass spectral data for the following selected characteristic ions: M/Z 257, 320, and 322 for unlabeled 2,3,7,8-TCDD; M/Z 328 for 2,3,7,8-TCDD-$^{37}Cl_4$; and M/Z 332 and 334 for 2,3,7,8-TCDD-$^{13}C_{12}$. Use the same data acquisition time and MS operating conditions used to determine response factors.

As will be noted in Section 4, the results of these individual MM5 train analyses were that 2,3,7,8-TCDD was not detected in any individual MM5 train. However, the detection limits of the procedure used were not low enough to allow quantitating 99.9999 percent 2,3,7,8-TCDD DRE.

In an attempt to improve detection limits on a ng/dscm basis, the extracts from the four MM5 trains operated simulatneously at the E-duct location were combined subsequent to the individual extract analyses and these pooled extracts analyzed for 2,3,7,8-TCDD. In these analyses, performed at the CRF, the pooled extracts were again subjected to the above extract cleanup procedures, concentrated to 50 µl, then analyzed by HRGC/LRMS for 2,3,7,8-TCDD in accordance with Method 8280 (revision dated May 12, 1986) procedures. The choices for GC capillary column (60m, DB-5), GC temperature program, and selective ion monitoring schedule were taken from (4).

3.2.4 Analysis of Samples to Determine HCl Emissions

Monitoring of flue gas for hydrogen chloride was performed using two methods: the continuous HCl monitor discussed in Section 3.1, and by analysis of the MM5 train impinger solutions for collected chlorides as outlined in the following.

Aliquots (0.5 ml) of the MM5 impinger condensate were analyzed with an Orion Research Model 601A digital ionalyzer. Chloride ion measurements of 5-ml aliquots of the MM5 condensate were made with a specific ion electrode and digital pH meter with expanded millivolt scale. A 1-mv change in potential corresponded to a 4-percent change in concentration when this monovalent ion was being measured.

3.2.5 Preparation and Analysis of Preburn and Feed Waste Samples

For the waste samples, 1-g aliquots were weighted out and spiked with 100 ng of 1,2,3,4-TCDD-$^{13}C_{12}$, 50 ng of 2,3,7,8-TCDD-$^{13}C_{12}$, and 10 ng of 2,3,7,8-TCDD-$^{37}Cl_4$. Six ml of methanol and 4 ml of benzene were added to each aliquot. Then 200 µl of the aliquot was diluted to 1 ml with hexane.

Standard extract cleanup procedures included multilayer acid/base silica gel (Davison Type 60, 70-230 mesh) column and acidic alumina (Fisher activate 1, 80-200 mesh) gravity column chromatography and Carbopack C

(Supelco 80-100 mesh) column. After the sample cleanup, the aliquots were concentrated to 50 µl.

The samples were analyzed for 2,3,7,8-TCDD on a Finnigan 4000 HRGC/LRMS. The column used was a SP-2330 60-m fused silica capillary column.

The samples were also analyzed for the halogenated volatile organic priority pollutants by Method 8010, and for the semivolatile organic priority pollutants by Method 8270.

3.2.6 Procedures for Physical Characterization of Waste

Bulk density of the waste was determined by measuring the weight of a known volume of this material at 20°C. Determination of heat of combustion was by bomb colorimeter in accordance with ASTM D 240-76. Determination of total solid and ash content was in accordance with protocols outlined in EPA/SW-846, 2nd Edition, July 1982.

3.2.7 Procedures for the Elemental Analysis of Waste and Water Samples

One sample of the waste and duplicate samples of the scrubber blowdown water were forwarded to an outside laboratory for priority pollutant trace element analysis. The methods used are summarized in Table 11. The waste sample was acid digested in accordance with Method 3030, prior to analysis.

TABLE 11. ELEMENTAL ANALYSIS PROCEDURES USED

Element	Analysis principle	SW-846 Method
Antimony, Sb	Hydride Generation Atomic Absorption	7041
Arsenic, As	Hydride Generation Atomic Absorption	7061
Beryllium, Be	Inductively Coupled Argon Plasma	6010
Cadmium, Cd	Graphite Furnace Atomic Absorption	7131
Chromium, Cr	Graphite Furnace Atomic Absorption	7191
Copper, Cu	Graphite Furnace Atomic Absorption	7211
Lead, Pb	Graphite Furnace Atomic Absorption	7421
Mercury, Hg	Cold Vapor Hydride Generation Atomic Absorption	7470
Nickel, Ni	Graphite Furnace Atomic Absorption	7521
Selenium, Se	Hydride Generation Atomic Absorption	7741
Silver, Ag	Graphite Furnace Atomic Absorption	7761
Thallium, Tl	Graphite Furnace Atomic Absorption	7841
Zinc, Zn	Flame Atomic Absorption	7950

REFERENCES

3. "ASME MM5 Sampling Methodology for Chlorinated Organics," Draft No. 4, American Society of Mechanical Engineers, New York, October 1984.

4. "Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs)," ASME Environmental Standards Workshop, September 18, 1984.

SECTION 4

TEST RESULTS

Results of the tests performed are discussed in this section. The initial background burn results are presented in Section 4.1; Section 4.2 describes results from the miniburn performed on September 9; full-burn test results (September 20 and 21) are discussed in Section 4.3; calculated waste destruction and removal efficiencies are discussed in Section 4.4; and analysis results for the incinerator ash and scrubber blowdown are presented in Section 4.5.

4.1 BACKGROUND BURN

Figure 11 shows the continuous monitor data for the background burn tests performed on September 4, 1985. The data plotted represent twenty minute to hourly averages over the time period at the point plotted. Data taken at both the afterburner exit and the stack are shown. During this test, instrument malfunctions necessitated that CO_2 and O_2 be monitored by one instrument for each parameter on a time-share basis. Thus, only afterburner data for CO_2 and O_2 were recorded before 1300, and only stack data were recorded after 1300. Problems with one NO_x analyzer limited data acquisition for that parameter to the afterburner exit only. Problems with one CO instrument limited the acquisition of CO data to the stack. Neither THC nor HCl levels were monitored during this test.

The data in Figure 11 show that O_2 and CO_2 levels at the afterburner exit averaged about 15 percent and 8 percent, respectively. NO_x levels at this location were generally below 40 ppm.

At the stack, O_2 and CO_2 levels were about 17 percent and 7 percent, respectively, from 1300 to 1900. Levels of CO in the stack were recorded as zero throughout the test, which suggests they were quite low, <10 ppm.

As noted in Section 3.1, MM5 sampling for particulate emissions and POHC (2,3,7,8-TCDD) emissions was performed at the kiln exit, the afterburner exit, in the E-duct (the horizontal transfer duct between the packed tower scrubber exit and the carbon-bed absorber), and at the stack (downstream of the ID fan). Two trains were run at each of the kiln exit, afterburner exit, and stack locations. Four trains were run in the E-duct. Corresponding sampling periods for each train were noted in Figure 11. As shown, all trains ran uninterrupted for 8 to 10 hours except the one in the stack south port.

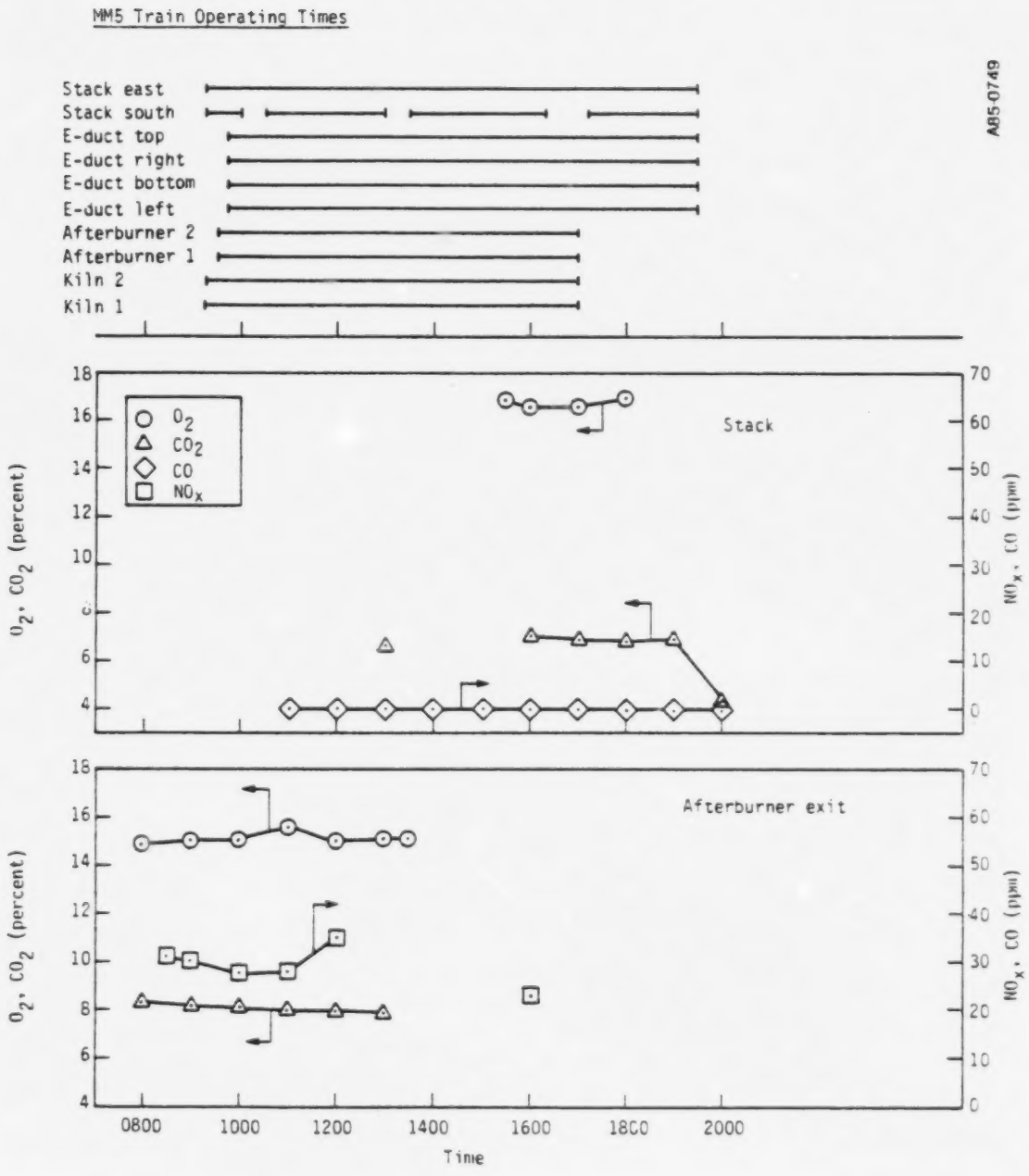


Figure 11. Emission monitor data: background burn of September 4, 1985.

Particulate and 2,3,7,8-TCDD emission results are summarized in Table 12, along with results of the percent isokinetic calculation for each train for which this parameter is applicable (no attempt at performing isokinetic sampling nor duct traversing was made for the trains operated at the kiln and afterburner exits). As indicated in Table 12, the percent isokinetic values for the trains run at the E-duct and stack locations varied from 62 to 101 percent. Only two trains were within the Method 5 specified acceptable range of 90 to 110 percent. Those trains failing this criterion failed on the low side (percent I <90). This means that the velocity of the sample entering the probe nozzle was, on average, less than that of the combustion gas sampled. The reason for these low values was that excessive pressure drop across the glass frit in the condenser/resin cartridge of the sampling train was frequently experienced. Thus, particulate emission levels measured are likely to be slightly lower than those actually present.

The data in Table 12 suggest that particulate levels in the kiln and afterburner exit were in the 0.3- to 3-mg/dscm range as measured, or 2 to 8 mg/dscm at 7-percent O_2. At the stack exit particulate levels may have been in the 2-mg/dscm range, or 8 mg/dscm at 7-percent O_2, although there was quite a difference in the measured loading between the two trains run. In any event, emissions were well below the 180 mg/dscm corrected to 7-percent O_2 limit in the CRF Part B permit.

Dioxin levels measured were less than detectable in all trains. This is as would be expected for the background burn. Detection limits in the E-duct and stack were in the 0.1 to 0.3-ng/dscm range.

4.2 MINIBURN

Figure 12 shows the continuous monitor data for the mini waste burn performed on September 9, 1985. Again, data taken at both the afterburner exit and the stack are shown. During this test, instrument problems required that O_2 in the stack and afterburner be monitored on a time-share basis. Thus, O_2 was measured at the afterburner exit from 0900 to 1500, and at the stack from 1500 to 2000. The instrument used to monitor NO_x in the stack was hampered by a leak. As a consequence, no data were available until 1500, and none were taken after 1700. A problem with the instrument monitoring CO_2 in the stack reduced the amount of useful data from the sampling location, such that no information was available after 1100. Instrument problems also limited CO data to the afterburner exit location. The THC monitor was also not run during this test.

Superimposed onto Figure 12 is the measured waste feedrate for the test duration, as well as an indication of when sampling trains were run. For these tests, sampling train cooling system problems prevented performing MM5 sampling at both the E-duct and stack locations. Sampling at the kiln exit (two trains) and at the afterburner exit (two trains) was performed, however.

The data in Figure 12 show that afterburner exit CO_2 fluctuated between 6 and 7 percent. Afterburner exit O_2 increased from about 12 percent at 1530

TABLE 12. PARTICULATE AND 2,3,7,8-TCDD EMISSIONS: BACKGROUND BURN OF SEPTEMBER 4, 1985

Sampling location	Volume sampled (dscm)	Percent isokinetic	Particulate weight (mg)	Particulate emissions		Total 2,3,7,8-TCDD collected (ng/train)	2,3,7,8-TCDD emissions (ng/dscm)
				As measured (mg/dscm)	Corrected to 7-percent O_2 (mg/dscm)		
Kiln exit							
Train 1	6.46	--	1.8	0.28		<6.6	<0.95
Train 2	6.85	--	3.4	0.50		<2.5	<0.36
Afterburner exit							
Train 1	6.89	--	5.7	0.83	1.9[b]	<12	<1.7
Train 2	6.16	--	20.8	3.4	7.9[b]	<2.6	<0.43
E-duct							
Top train	6.58	81.0	--[a]			<1.2	<0.18
Bottom train	9.84	101.5	--[a]			<2.3	<0.24
Left train	7.60	82.7	--[a]			<2.3	<0.31
Right train	6.31	65.9	--[a]			<2.0	<0.31
Stack							
East train	9.77	62.4	18.3	2.3	8.1[c]	<2.0	<0.21
South train	8.78	97.6	3.1	0.4	1.4[c]	<0.94	<0.10

[a]Particulate weights not measured, no filters were used in the E-duct trains for this test.
[b]Corrected from 15-percent O_2 to 7-percent O_2.
[c]Corrected from 17-percent O_2 to 7-percent O_2.

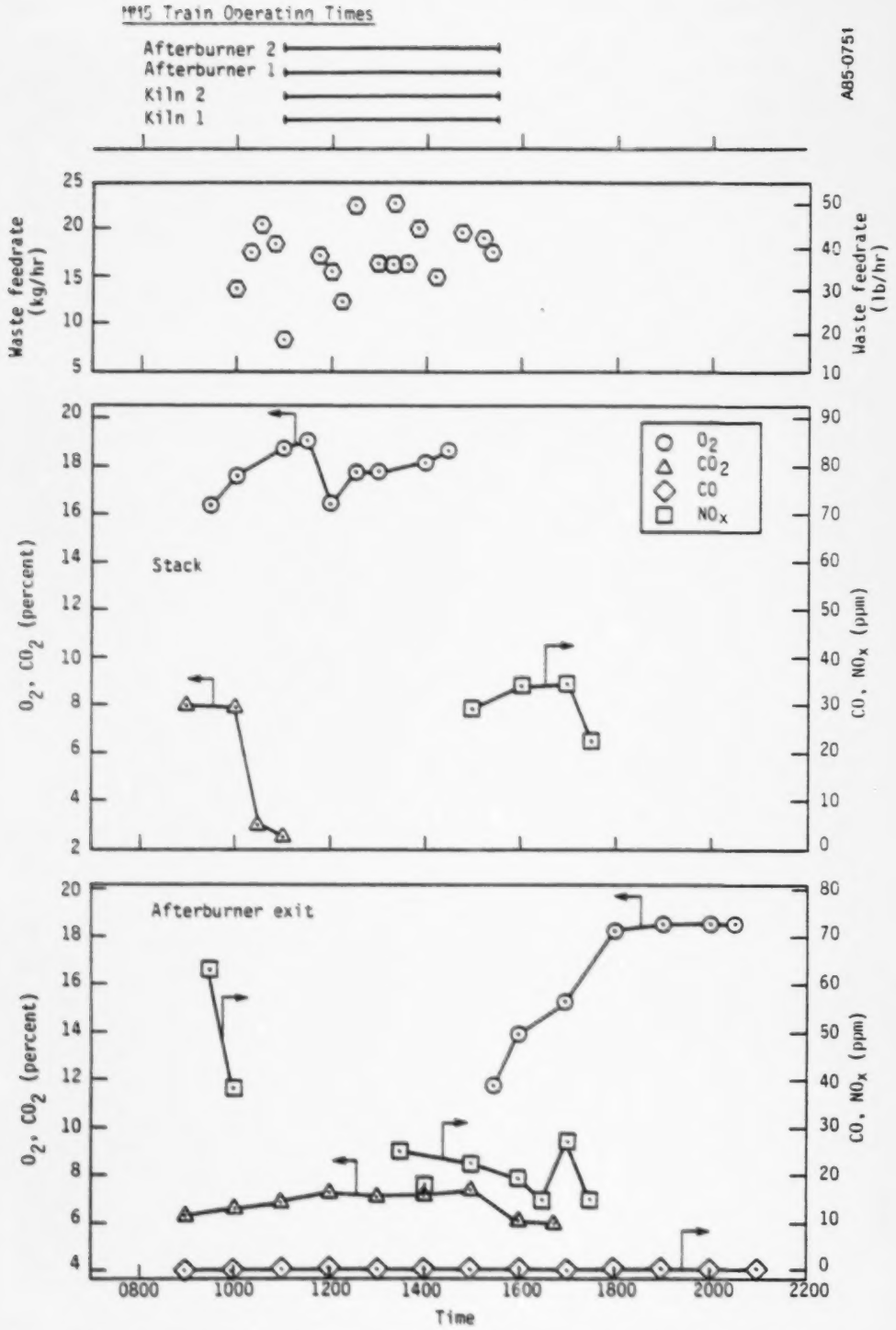


Figure 12. Emission monitor data: miniburn of September 9, 1985.

to over 18 percent after 1800. NO_x levels at the afterburner exit were generally below 70 ppm. CO levels were also measured at zero during this test, implying that they were less than 10 ppm. At the stack, O_2 levels fluctuated between 16 and 19 percent up until 1500 when the location was changed to sampling at the afterburner exit. NO_x levels at the stack were in the 20- to 35-ppm range for the brief period of time they were measured.

Particulate and 2,3,7,8-TCDD emission results for these tests from the kiln and afterburner exit trains are summarized in Table 13. Recall that these trains did not sample isokinetically, so particulate levels should be considered only approximate. The data suggest that particulate levels were in the 200- to 500-mg/dscm range in the kiln transfer duct and in the 600- to 2000-mg/dscm range at the afterburner exit. Since no E-duct or stack sampling was successful for this test, a determination as to whether compliance with a permit level of 180 mg/dscm at 7-percent O_2 could not be made.

Dioxin levels measured at both the kiln and afterburner exit for this test were also less than detectable, and at detection limits comparable to, to an order of magnitude higher than were realized during the background burn (e.g., about 1 to 10 ng/dscm for this test).

HCl emissions were measured using the continuous CEA HCl monitor at the E-duct location for these tests. The average concentration over the test period was 360 ppm, which corresponds to 0.54-g/dscm HCl. Afterburner exit flue gas flowrate was about 14 dscm/min for this test (see Section 4.4; no

TABLE 13. PARTICULATE AND 2,3,7,8-TCDD EMISSIONS: MINIBURN OF SEPTEMBER 9, 1985

Sampling location	Volume sampled (dscm)	Particulate weight (mg)	Particulate level (mg/dscm)	Total 2,3,7,8-TCDD collected (ng/train)	2,3,7,8-TCDD level (ng/dscm)
Kiln exit					
Train 1	1.89	876.7	463	<1.4	<0.74
Train 2	1.44	257.5	175	<2.0	<1.4
Afterburner exit					
Train 1	1.24	723.6	585	<16.3	<13
Train 2	0.57	1159.2	2030	<6.2	<11

E-duct flowrate measurement was made since the Method 5 trains were not operated). If this were the E-duct gas flowrate, then the E-duct HCl flowrate would have been about 0.45 kg/hr. This is below the CRF Part B emission level of 0.5 kg/hr. However, clear compliance with the permit requirement would have been better demonstrated if an actual E-duct flue gas flowrate had been obtained.

4.3 FULL BURN

Figure 13 shows the continuous monitor data for the first full waste burn performed on September 20, 1985. Figure 14 shows analogous data for the second full waste burn performed on September 21. As for previous tests, data were taken both at the afterburner exit and at the stack. Data from both locations are shown in Figures 13 and 14.

Continuing difficulties with the continuous emission monitor systems limited stack data to CO_2 levels only on September 20, although the full complement of instruments was available at the afterburner for most of the test on September 20. As shown in Figure 13, stack CO_2 averaged about 8 percent over the test, although stack CO_2 apparently steadily decreased from about 9 percent at the beginning of the test to just below 8 percent near the end of the test. This steady decrease parallels a steady decrease in the nominal waste feedrate over the test, which is also shown in Figure 13. Nominal waste feedrate steadily decreased from the 15- to 25-kg/hr range early in the test to below 5 kg/hr near the end of the test. Interestingly, a sharp drop in waste feedrate to zero in the middle of the test (at about 1500) is accompanied by an abrupt, though slight, decrease in stack CO_2.

Afterburner exit O_2 and CO_2 were quite variable over the test, with O_2 ranging from 6 to 12 percent and CO_2 ranging from 2 to 7 percent. The fact that the O_2 and CO_2 traces at the afterburner exit were parallel early in the test (both decreasing or both increasing in parallel) is highly suspicious. This implies that one (or both) monitors was reading erroneously. Further disturbing is the fact that stack CO_2 readings were greater than afterburner exit levels over much of the test. The reverse is expected owing to air inleakage between the two sampling locations. The fact that the afterburner exit measured level was lower suggests that there was an air inleak in the sample transfer line to the analyzer. NO_x emissions at the afterburner exit were generally below 15 ppm for most of the test. The CO monitor read zero at the afterburner exit for the entire test, suggesting that CO levels at this location were less than 10 ppm.

The instrument problems in the analyzer system dedicated to the stack location which existed on September 20 persisted into September 21. However, for this test the afterburner exit O_2 monitor was switched to monitoring stack gas at just about the time the flue gas sampling trains were started. Thus, as illustrated in Figure 14, O_2 and CO_2 data were obtained at the stack for the test duration, and CO_2, CO, and NO_x data were obtained at the afterburner exit over much of the test.

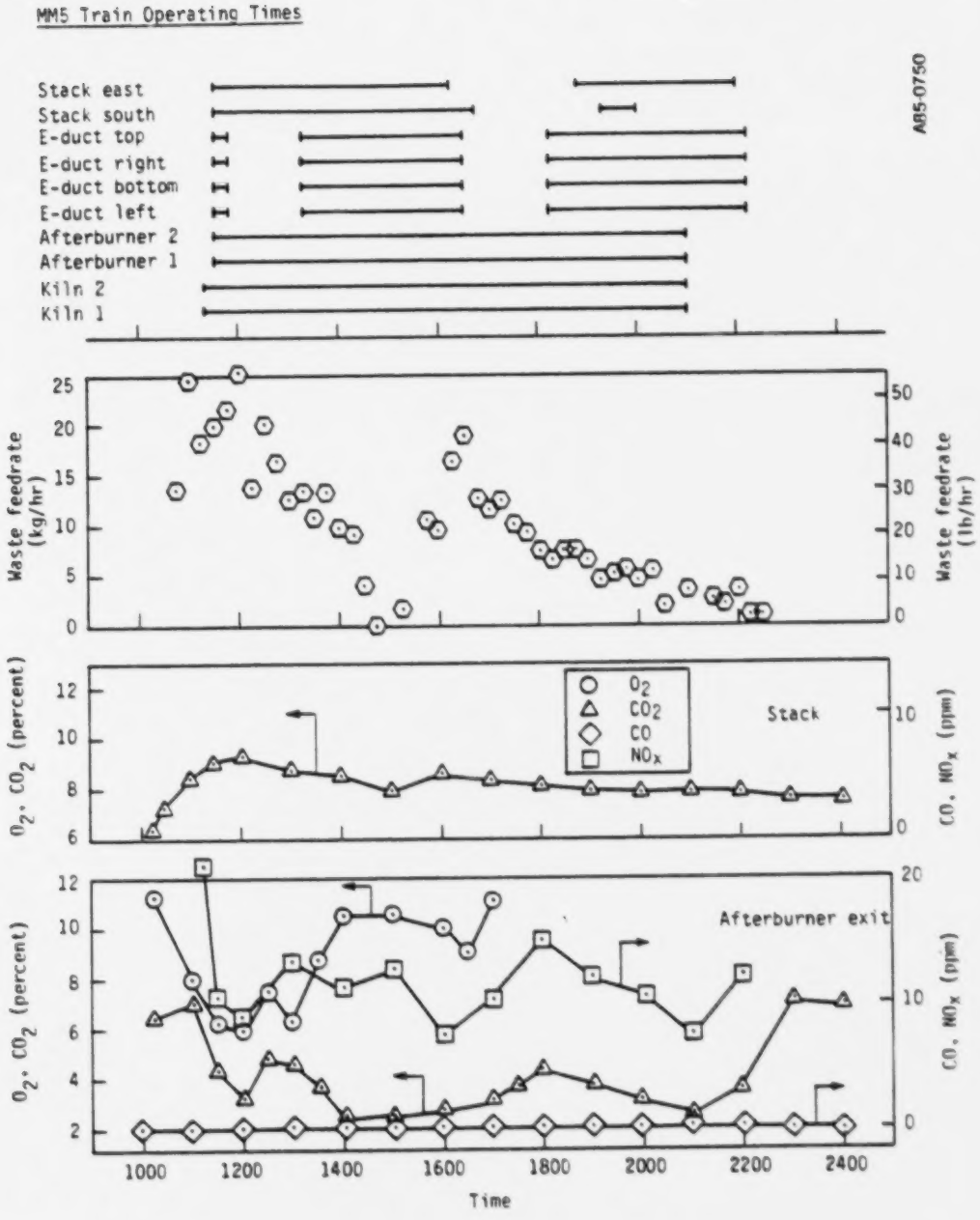


Figure 13. Emission monitor data: full burn of September 20, 1985.

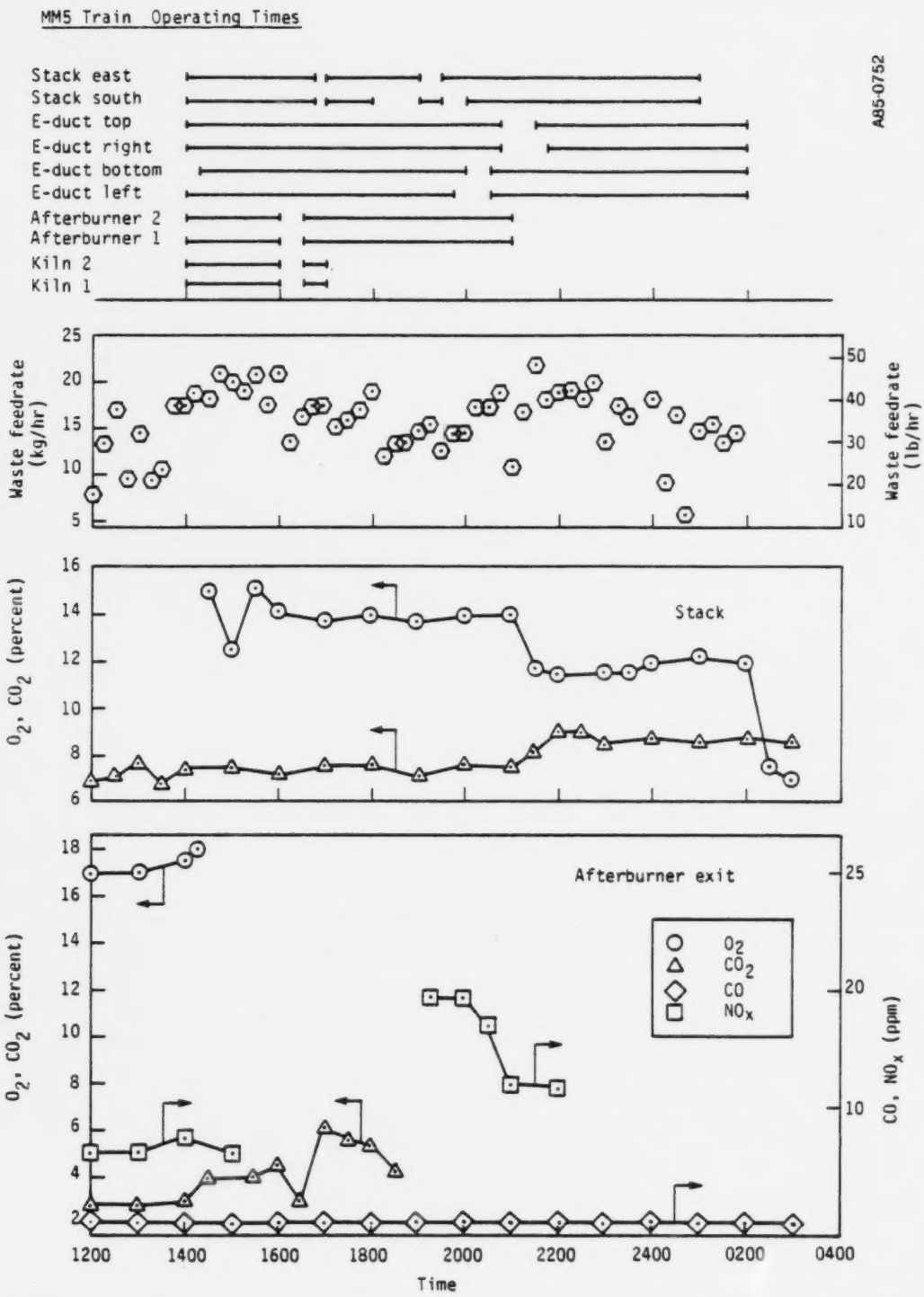


Figure 14. Emission monitor data: full burn of September 21, 1985.

Figure 14 shows that stack O_2 and CO_2 levels were about 14 and 7.5 percent, respectively, early in the test, with a relatively abrupt change to about 12 and 8.8 percent, respectively, late in the test. At the afterburner exit, CO_2 levels varied about 4 percent early in the test, over the period during which the monitor was operational. Again, the fact that stack CO_2 levels were higher than afterburner exit CO_2 levels is disturbing and suggests a continuing air inleak in the afterburner exit sample transfer line. Afterburner exit NO_x levels were less than 20 ppm throughout the test for the periods they were monitored.

THC levels were measured both at the inlet and outlet of the carbon-bed absorber during the September 20 test (continuing instrument problems prevented obtaining data on September 21). These data are shown in Figure 15. As indicated, the THC levels at the carbon-bed inlet were essentially level at 5 ppm until about 1900 when there was an apparent decrease to 2 ppm. This apparent decrease was due to an instrument calibration check, however, and not reflective of a real change in flue gas concentrations. Carbon-bed inlet THC levels did spike once to 27 ppm at 1630. THC levels at the carbon-bed outlet were about 4 ppm until 1400, decreasing to 2.5 ppm until 1900. There was a further apparent decrease to below 1 ppm at 1900, but this again was due to an instrument calibration adjustment. Of course, all these levels are quite low, near the quantitation limit of the analyzer used.

Particulate and 2,3,7,8-TCDD emission results from the full waste burn test of September 20 are summarized in Table 14, along with results of the percent isokinetic calculations for the E-duct and stack trains (the only ones for which duct traversing and sampling velocity adjustments were made). An analogous summary for the full waste burn test of September 21 is given in Table 15. As indicated in Table 14, the percent isokinetic values for the trains run in the E-duct and the stack for the test on September 20, ranged from 72 to 94.5 percent. Only for two trains was the percent isokinetic value between the 90 to 110 percent requirements for an approved particulate load measurement via Method 5. The reason for the low values again was excessive pressure drop in the condenser/resin cartridge of the train due to plugging of the glass frit in this cartridge as noted in Section 4.1.

These deficiencies aside, particulate levels in the E-duct were 343 mg/dscm based on averaging the levels measured by all four trains. Given that the flue gas O_2 level at this location was liable to be in the 10-percent range (see Figure 13, afterburner exit), particulate levels at this location, were they direct emissions to the atmosphere, would exceed the RCRA hazardous waste incinerator performance standard of 180 mg/dscm corrected to 7-percent O_2. However, levels measured at the stack location, downstream of the carbon-bed/HEPA filter, were 47 mg/dscm (average of the two trains operated at that location). Although no stack O_2 data were available at this location for correcting emissions to 7-percent O_2, if stack O_2 levels were less than 17.3 percent, then particulate emissions would have been less than 180 mg/dscm corrected to 7-percent O_2. Since afterburner exit O_2 levels were less than 11 percent for these tests, it is expected that stack O_2 levels certainly were less than 17 percent, thus particulate emission levels

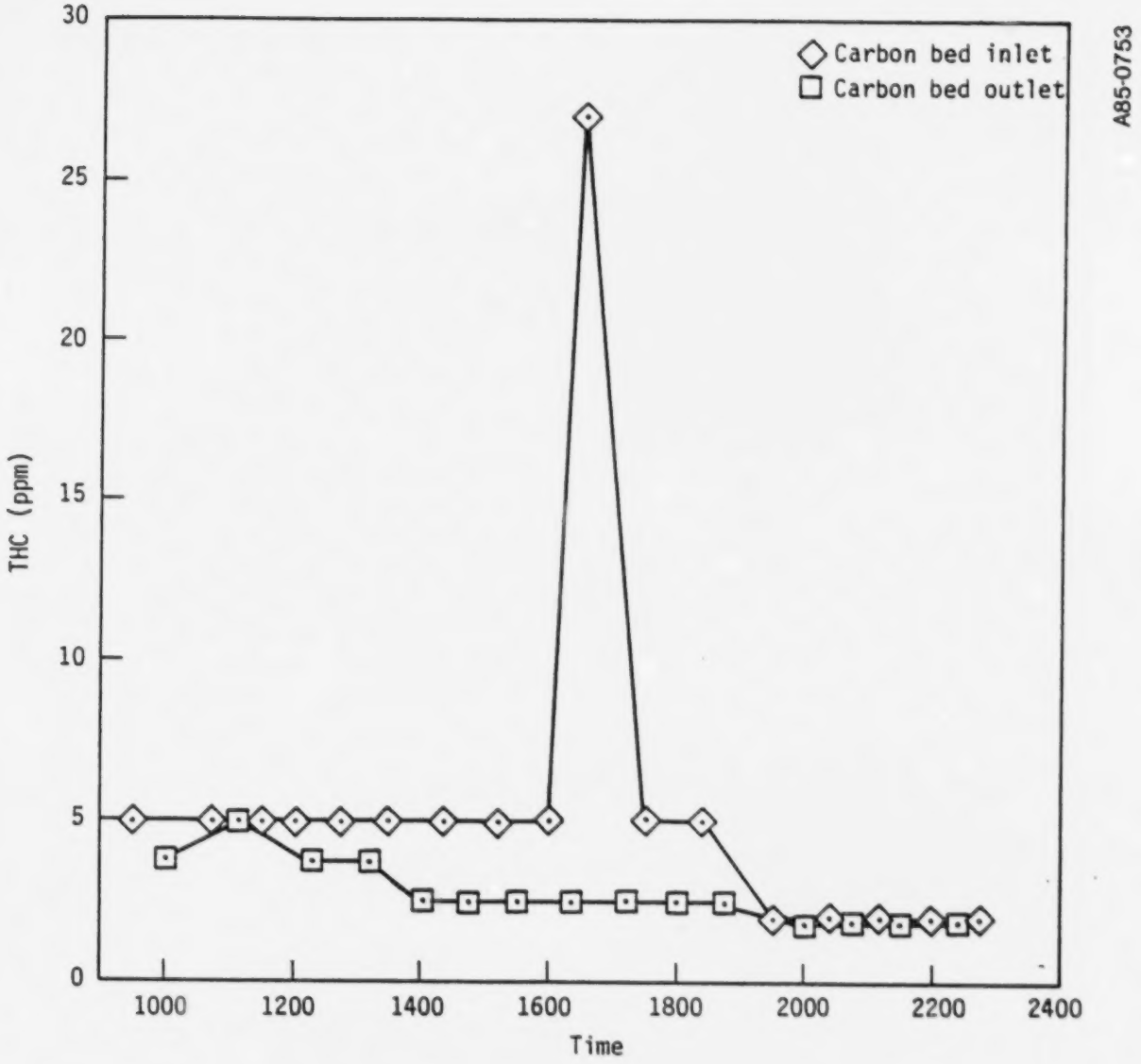


Figure 15. THC monitor data: full burn of September 20, 1985.

TABLE 14. PARTICULATE AND 2,3,7,8-TCDD EMISSIONS: FULL BURN OF SEPTEMBER 20, 1985

Sampling location	Volume sampled (dscm)	Percent isokinetic	Particulate weight (mg)	Particulate emissions as measured (mg/dscm)	Total 2,3,7,8-TCDD collected (ng/train)	2,3,7,8-TCDD emissions (ng/dscm)
Kiln exit						
Train 1	4.36	--	11.8	2.71	<2.4	<0.55
Train 2	7.53	--	11.0	1.46	<1.3	<0.17
Average				2.09		
Afterburner exit						
Train 1	1.41	--	522.8	371	<5.3	<3.8
Train 2	3.34	--	10.5	--[a]	<4.2	<1.3
E-duct						
Top train	6.82	94.5	796.5	266[b]	<2.9	<0.43
Bottom train	4.31	73.4	829.3	564[b]	<2.2	<0.51
Right train	5.13	62.0	564.3	291[b]	<12.7	<2.5
Left train	5.64	88.5	511.4	251[b]	<3.1	<0.55
Average				343		
Stack						
East train	7.42	93.7	284.8	38.4	<16.8	<2.3
South train	6.31	74.5	353.5	56.0	<9.3	<1.5
Average				47.2		

[a]Evidence of significant leak in the sampling train was discovered after sampling was complete. Data considered invalid for particulate measurements.
[b]Train filters removed prior to the completion of sampling; volumes sampled with filters in place were 3.0, 1.47, 1.94, and 2.01 dscm, respectively, for the top, bottom, right, and left trains, respectively.

TABLE 15. PARTICULATE AND 2,3,7,8-TCDD EMISSIONS: FULL BURN OF SEPTEMBER 21, 1985

Sampling location	Volume sampled (dscm)	Percent isokinetic	Particulate weight (mg)	Particulate emissions		Total 2,3,7,8-TCDD collected (ng/train)	2,3,7,8-TCDD emissions (ng/dscm)
				As measured (mg/dscm)	Corrected to 7-percent O_2 (mg/dscm)		
Kiln exit							
Train 1	1.01	--	762.3	753		<6.5	<6.4
Train 2	0.35	--	670.0	1940		<7.2	<21
Afterburner exit							
Train 1	3.90	--	598.9	154		<15.0	<3.9
Train 2	2.58	--	512.5	199		<7.3	<2.8
Average				176			
E-duct							
Top train	6.72	47.9	<1	<0.15		<12.9	<1.9
Bottom train	5.97	31.2	13.6	2.3		<12.0	<2.0
Right train	5.50	37.4	59.6	10.8		<12.3	<2.2
Left train	7.59	40.6	<1	<0.13		<5.8	<0.76
Stack							
East train	5.68	53.2	412.0	72.6	132[a]	<8.3	<1.5
South train	2.78	44.1	577.7	208	378[a]	<4.5	<1.6
Average				140	255		

[a]Corrected to 7-percent O_2 from an average stack O_2 level of 13.3 percent, see Figure 4-4.

should have been in compliance with the CRF Part B particulate emission limit.

As in previous tests in this series, dioxin levels were less than detectable in all individual train extracts analyzed. The data in Table 14 suggest that dioxin (2,3,7,8-TCDD) levels were less than about 0.5 ng/dscm at the kiln exit and in the E-duct, less than the 1- to 4-ng/dscm range at the afterburner exit, and less than about 2 ng/dscm in the stack. DRE implications of these results are discussed in Section 4.4.

The data in Table 15 show that the attempts to perform isokinetic sampling in the full waste test burn on September 21 were less successful than those in the tests on September 20. The percent isokinetic values for the E-duct and stack trains ranged from 31 to 53 percent during this second set of tests. In addition, many other problems were associated with obtaining particulate levels in the E-duct for this test. In fact, two MM5 train filters actually apparently lost weight after sampling. As a result, the particulate loading data at this location are not considered reliable in the slightest.

Particulate emissions at the stack were 140 mg/dscm as measured (average of the two trains operated at this location), or 255 ng/dscm corrected to 7-percent O_2. This level is greater than the RCRA hazardous waste incinerator particulate emission standard and the CRF Part B permit emission standard of 180 ng/dscm at 7-percent O_2.

Again no dioxin levels were found above method detection limits in the combined (single train) extracts from any sampling train run. Thus dioxin levels were less than 4 ng/dscm at the afterburner exit, less than 2 ng/dscm in the E-duct, and less than 1.5 ng/dscm in the stack. Section 4.4 discusses the DRE implications of these results.

HCl levels in the E-duct were measured via two techniques during the test on September 20. These were by way of the CEA continuous HCl monitor described in Section 3.1, and by analyzing the MM5 train impinger solutions for captured chloride via specific ion electrode. The average CEA analyzer reading over the test period was 160 ppm HCl, which corresponds to 0.25 g/dscm. The HCl levels in the E-duct as determined by the MM5 train impinger solution analyses were 0.21, 0.22, 0.31, and 0.29 g/dscm for the top, right, bottom, and left trains, respectively. Thus, the average MM5 train value was also 0.26 g/dscm HCl. The E-duct flue gas flowrate was between 13 and 18 dscm/min (see Section 4.4), depending on whether more trust was placed in a Method 5-related velocity traverse (18 dscm/min) or the helium tracer system measure (13 dscm/min). Thus, E-duct HCl flowrates, at 0.26 g/dscm concentration, were between 0.2 and 0.25 kg/hr. If these were stack emission rates (stack emissions should be the same as E-duct flowrates), then they were well below the CRF Part B permit requirement of 0.5 kg/hr.

4.4 DIOXIN DREs

DREs for POHCs in a trial burn such as the ones performed in this study are typically calculated by dividing the flue gas mass flowrate of POHC (as determined by the flue gas sampling procedure used) by the mass flowrate of POHC fed to the incinerator (as determined by the waste feedrate and the waste POHC concentration), subtracting this value from 1.0 and multiplying the result by 100 (to give a percent value). However, as illustrated by the data shown in Figure 12, 13, and 14, the waste feedrate varied considerably over the duration of each test performed. As a consequence, a slightly different procedure was used to calculate DREs for this set of tests. Instead of using waste feedrates and flue gas emission rates, the total quantity of waste (POHC) fed during the period of time a given sampling train was in operation was divided by the total expected amount of POHC emitted over that time as calculated from the sampling train data, and this ratio subtracted from 1.0 and multiplied by 100.

The total amount of waste fed over a given sampling interval was taken directly from the waste Tote tank scale readings recorded over time. Results of the analysis of three waste samples taken before and during the tests showed 2,3,7,8-TCDD concentrations of 32, 29, and 49 µg/g waste, for an average of 37 µg/g.

The total amount of POHCs emitted was calculated from the concentration, as measured by the respective sampling train, multiplied by an estimated flue gas flowrate and by the period of time the respective sampling train was in operation. The estimated flue gas flowrate was obtained via two methods. The first was from the MM5 train flue gas velocity measurement, which was used for all sampling locations. The second was from the helium tracer data which allowed a backup calculation at the E-duct and stack sampling locations.

DRE results calculated via these methods are shown in Table 16 for the miniburn of September 9, in Table 17 for the full burn of September 20, and in Table 18 for the full burn of September 21.

The data in Table 16 shows that the detection limits achieved in samples from the kiln exit sampling trains allowed establishing that 2,3,7,8-TCDD destruction efficiency (DE) was greater than 99.9999 percent in the kiln for the miniburn performed on September 9. The poorer detection limits achieved in afterburner exit sampling trains, combined with increased flue gas flowrate at this location, resulted in the ability only to establish combined kiln/afterburner DE of greater than 99.9998 percent.

Table 17 suggests similar conclusions from the full burn tests of September 20. Again DE of greater than 99.9999 percent was apparent at the kiln exit. However, only greater than 99.999 percent DE could be established at the afterburner exit. Good detection capabilities in three of the four individual E-duct trains suggest that incinerator system (kiln, afterburner, and APCD) DRE was greater than 99.9998 percent regardless of which flue gas flowrate measure is used (the helium tracer method flue gas flowrate value

TABLE 16. 2,3,7,8-TCDD DREs: MINIBURN OF SEPTEMBER 9, 1985

Sampling location	Total amount of waste fed (kg)	Total amount of 2,3,7,8-TCDD fed[a] (g)	Sampling period duration (min)	Flue gas 2,3,7,8-TCDD concentration (ng/dscm)	Based on helium tracer data: Flue gas flowrate (dscm/min)	Based on helium tracer data: Total 2,3,7,8-TCDD emitted (µg)	Based on helium tracer data: DRE (percent)
Kiln exit							
Train 1	77	2.9	261	<0.74	7.5	<1.4	>99.99995
Train 2	77	2.9	261	<1.4	7.5	<2.7	>99.99991
Afterburner exit							
Train 1	77	2.9	261	<13	13.7	<46	>99.9984
Train 2	77	2.9	261	<11	13.7	<39	>99.9986

[a]Based on waste 2,3,7,8-TCDD concentration of 37 µg/g.

TABLE 17. 2,3,7,8-TCDD DREs: FULL WASTE BURN OF SEPTEMBER 20, 1985

Sampling location	Total amount of waste fed (kg)	Total amount of 2,3,7,8-TCDD fed[a] (g)	Sampling period duration (min)	Flue gas 2,3,7,8-TCDD concentration (ng/dscm)	Based on helium tracer data			Based on flue gas velocity data		
					Flue gas flowrate (dscm/min)	Total 2,3,7,8-TCDD emitted (μg)	DRE (percent)	Flue gas flowrate (dscm/min)	Total 2,3,7,8-TCDD emitted (μg)	DRE (percent)
Kiln exit										
Train 1	91	3.4	570	<0.55	8.2	<2.6	>99.99992	--	--	--
Train 2	91	3.4	570	<0.17	8.2	<0.79	>99.99998	--	--	--
Afterburner exit										
Train 1	91	3.4	570	<3.8	15.1	<32	>99.99903	--	--	--
Train 2	91	3.4	570	<1.3	15.1	<11	>99.99967	--	--	--
E-duct										
Top train	52	2.0	450	<0.43	18.1	<3.5	>99.99982	13.1	<2.5	>99.99987
Bottom train	52	2.0	450	<0.51	18.1	<4.1	>99.99979	13.1	<3.0	>99.99985
Right train	52	2.0	450	<2.5	18.1	<20	>99.99896	13.1	<15	>99.99925
Left train	52	2.0	450	<0.55	18.1	<4.5	>99.99977	13.1	<3.2	>99.99983
Stack										
East train	62	2.3	460	<2.3	20.2	<21	>99.99907	18.3	<19	>99.99916
South train	70	2.6	470	<1.5	20.2	<14	>99.99945	18.3	<13	>99.99951

[a]Based on waste 2,3,7,8-TCDD concentration of 37 μg/g.

differs from the Method 5 pitot tube velocity traverse value by 20 to 30 percent at the E-duct, as discussed in Section 2.3; this difference would not measurably affect DRE, e.g., the difference between 99.9998 and 99.9999 percent DRE corresponds to a factor of 2 difference in flue gas flowrate estimate). Poorer detection limits for the stack trains allowed only establishing final (full system) DRE of greater than 99.999 percent.

Table 18 again shows similar conclusions for the full burn performed on September 21. Here the data suggest incinerator system 2,3,7,8-TCDD DRE of greater than 99.9997 percent in both the E-duct and the stack.

The current regulations for dioxin destruction via incineration require 99.9999 percent DRE. Accordingly, the objective of these tests was to investigate whether this level could be achieved. Based on the single train results presented in Tables 16 through 18, it can be stated that, in all likelihood, 99.9999 percent DRE was achieved. However, clear demonstration of this was not possible on an individual train basis due to method detectability limitations.

In an attempt to lower detection limits to be able to make an unambiguous 99.9999 percent DRE capability statement, the extracts from the four E-duct trains for each full burn test were combined, further concentrated, and subjected to method cleanup procedures. These further concentrated, pooled extracts were analyzed via HRGC/LRMS for 2,3,7,8-TCDD. Results from these analyses for the September 21 full burn are summarized in Table 19. As shown in the table, 2,3,7,8-TCDD was not detected even in the combined extract from the four MM5 trains operated at this location for this test. Results from the pooled September 21 test E-duct MM5 train extracts show that about 99.99999 percent DRE was achieved upstream of the carbon bed absorber for this test. This is an order of magnitude greater than the required 99.9999 percent DRE.

The usefulness of data from the pooled E-duct trains taken September 20 is severely compromised due to a spiking error which occurred during the offsite preparation of these extracts. A 10- to 15-fold excess of a recovery standard $^{13}C_{12}$-1,2,3,4-TCDD, was added to each of these extracts. Injection of such gross quantities of this compound saturates the mass spectrometer and overloads the capillary GC column within the retention time window of native 2,3,7,8-TCDD, precluding measurements of this analyte at low levels. As a consequence, the detection limits for pooled extracts (ng/dscm of flue gas) are not significantly below those for individual train extracts, thus little more can be said regarding 2,3,7,8-TCDD DRE for this test beyond conclusions stated in Table 17.

4.5 INCINERATOR ASH AND SCRUBBER BLOWDOWN ANALYSIS

Over the course of the three waste burns, approximately 26,500L (7000 gal) of scrubber blowdown was collected in two temporary storage tanks brought into the CRF specifically for this purpose. One tank contained about 15,100L (4000 gal) and the other about 11,400L (3000 gal). After the tests, two 2L samples of composited scrubber blowdown were collected. These were

TABLE 18. 2,3,7,8-TCDD DREs: FULL WASTE BURN OF SEPTEMBER 21, 1985

Sampling location	Total amount of waste fed (kg)	Total amount of 2,3,7,8-TCDD fed[a] (g)	Sampling period duration (min)	Flue gas 2,3,7,8-TCDD concentration (ng/dscm)	Based on helium tracer data: Flue gas flowrate (dscm/min)	Based on helium tracer data: Total 2,3,7,8-TCDD emitted (µg)	Based on helium tracer data: DRE (percent)	Based on flue gas velocity data: Flue gas flowrate (dscm/min)	Based on flue gas velocity data: Total 2,3,7,8-TCDD emitted (µg)	Based on flue gas velocity data: DRE (percent)
Kiln exit										
Train 1	45	1.6	140	<6.4	6.7	<6.0	>99.99964	--	--	--
Train 2	45	1.6	140	<21	6.7	<20	>99.99988	--	--	--
Afterburner exit										
Train 1	102	3.8	370	<3.9	11.5	<17	>99.99956	--	--	--
Train 2	102	3.8	370	<2.8	11.5	<12	>99.99969	--	--	--
E-duct										
Top train	174	6.4	650	<1.9	16.1	<20	>99.99969	13.4	<17	>99.99974
Bottom train	173	6.4	650	<2.0	16.1	<21	>99.99967	13.4	<17	>99.99973
Right train	174	6.4	650	<2.2	16.1	<23	>99.99864	13.4	<19	>99.99970
Left train	176	6.5	655	<0.76	16.1	<8.0	>99.99988	13.4	<6.7	>99.999897
Stack										
East train	164	6.1	595	<1.5	17.3	<15	>99.99975	17.6	<16	>99.99974
South train	150	5.5	535	<1.6	17.3	<15	>99.99973	17.6	<15	>99.99973

[a]Based on waste 2,3,7,8-TCDD concentration of 37 µg/g.

TABLE 19. 2,3,7,8-TCDD DREs BASED ON E-DUCT COMBINED MM5 TRAIN EXTRACTS

Test burn	Total amount of 2,3,7,8-TCDD fed (g)	Total volume sampled (dscm)	Total 2,3,7,8 collected (ng/4 trains)	2,3,7,8-TCDD emissions (ng/dscm)	Sampling period duration (min)	Based on helium tracer data: Flue gas flowrate (dscm/min)	Based on helium tracer data: Total 2,3,7,8-TCDD emitted (µg)	Based on helium tracer data: DRE (percent)	Based on flue gas velocity data: Flue gas flowrate (dscm)	Based on flue gas velocity data: Total 2,3,7,8-TCDD emitted (µg)	Based on flue gas velocity data: DRE (percent)
Full burn of 9/21/85	6.4	25.78	<1.7	<0.066	650	16.1	<0.69	>99.999989	13.4	<0.57	>99.999991

sampled from the top of each tank while contents were being recirculated. Sample containers for collection and shipment were rigorously cleaned at the Environmental Compliance Laboratory, Bay St. Louis, Mississippi (ECL-BSL).

In addition, a quantity of ash accumulated in the kiln ash pit over the duration of the experiments. Eight 50g samples of this ash were also collected.

Four ash samples were forwarded to Battelle-Columbus Laboratories for analysis of 2,3,7,8-tetra-, total tetra-, penta-, hexa-, hepta-, and octa-CDDs and CDFs via the methods noted in Section 3.2. The two water samples were forwarded to ECL-BCL for extraction and extract cleanup, with extracts in turn forwarded to the Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina (EMSL-RTP) for analogous PCDD/PCDF analysis. Results of these analyses are given in Tables 20 and 21. Values in parentheses in the tables reflect the method limit of detection for samples in which a particular chlorination class was not detected.

The data in Table 20 indicate that the kiln ash samples were devoid of tetra-, penta-, hexa-, hepta-, and octa-CDDs and CDFs with one possible exception (possible presence of octa-CDD). The data in Table 21 show that the scrubber blowdown water samples were also devoid of tetra-, penta-, hexa-, hepta-, and octa-CDDs and CDFs with the exception of octa-CDDs which were present at the 70 ppt level. This is not surprising since octa-CDDs are relatively common in environmental samples.

As noted in Section 3.2, the scrubber blowdown was also analyzed for the organic and trace element priority pollutants. Results of these analyses are summarized in Table 22. As shown in the table, none of the organic priority pollutants are present in the blowdown at levels above 100 ppm. In addition, none of the trace elements are present at concentrations which would cause the blowdown to be considered EP (Extraction Procedure) toxic. Based on all the analytical data, the blowdown would not be considered a hazardous waste.

TABLE 20. LEVELS OF PCDD AND PCDF IN KILN ASH SAMPLES

Analyte	Concentration[a] (ppt)[b]			
	Sample 1	Sample 2	Sample 3	Sample 4
2,3,7,8-TCDD	(13)	(10)	(5.6)	(28)
TCDDs-CDD	(13)	(10)	(5.6)	(28)
Penta-CDDs	(28)	(6.5)	(4.2)	(16)
Hexa-CCDs	(7.4)	(4.5)	(5.0)	(37)
Hepta-CDDs	(14)	(6.3)	(3.4)	(8.4)
Octa-CDDs	(44)	(18)	(15)	235
2,3,7,8-TCDF	(7.0)	(16)	(7.1)	(10)
TCDFs	(7.0)	(16)	(7.1)	(10)
Penta-CDFs	(11)	(2.7)	(1.7)	(6.4)
Hexa-CDFs	(4.6)	(2.8)	(3.1)	(7.4)
Hepta-CDFs	(12)	(6.2)	(3.4)	(8.4)
Octa-CDFs	(33)	(21)	(15)	(40)

[a]Numbers in parentheses denote analyte not detected to the detection limit noted in parentheses.
[b]1 ppt = 1 pg/g.

TABLE 21. PRIORITY POLLUTANT COMPOSITION OF THE SCRUBBER BLOWDOWN WATER

Analyte	Concentration[a] (ppt)[b]			
	Sample 1	Sample 1 duplicate	Sample 2	Sample 2 duplicate
2,3,7,8-TCDD	(0.005)	(0.02)	(0.02)	(0.04)
TCDDs-CDD	(0.06)	(0.08)	(0.09)	(0.09)
Penta-CDDs	(0.04)	(0.05)	(0.04)	(0.02)
Hexa-CCDs	(0.03)	(0.04)	(0.04)	(0.03)
Hepta-CDDs	(0.02)	(0.04)	(0.03)	(0.05)
Octa-CDDs	0.07	0.04	0.07	0.07
2,3,7,8-TCDF	(0.02)	(0.01)	(0.02)	(0.02)
TCDFs	(0.1)	(0.07)	(0.1)	(0.06)
Penta-CDFs	(0.02)	(0.02)	(0.07)	(0.03)
Hexa-CDFs	(0.02)	(0.06)	(0.06)	(0.06)
Hepta-CDFs	(0.1)	(0.02)	(0.03)	(0.03)
Octa-CDFs	(0.1)	(0.08)	(0.06)	(0.04)

[a]Numbers in parentheses denote analyte not detected to the detection limit noted in parentheses.
[b]1 ppt = 1 pg/ml.

TABLE 22. PRIORITY POLLUTANT COMPOSITION OF THE SCRUBBER BLOWDOWN WATER

Component	Concentration[a] (ppb, wt)	Detection limit (ppb, wt)
Volatile organic priority pollutants		
Methylene chloride	ND	12.6
1,1-dichloroethylene	ND	2.6
1,1-dichloroethane	6.1	2.6
t-1,2-dichloroethylene	ND	2.6
Chloroform	ND	4.2
1,2-dichloroethane	ND	5.0
1,1,1-trichloroethane	ND	2.6
Carbon tetrachloride	ND	2.6
Bromochloromethane	ND	4.2
1,2-dichloropropylene	ND	2.6
t-1,3-dichloropropylene	ND	5.0
Trichloroethylene	ND	2.6
Benzene	ND	2.6
1,1,2-trichloroethane	ND	6.8
Bromoform	ND	4.2
Tetrachloroethylene + tetrachloroethane	ND	5.0
Chlorobenzene	ND	12.6
Semivolatile organic priority pollutants		
All base/neutral semivolatile priority pollutants	ND	5
4-chloro--3-methylphenol	ND	50
2,4,6-trichlorophenol	ND	30
2,4-dinitrophenol	ND	30
4-nitrophenol	ND	50
2-methyl-4,6-dinitrophenol	ND	50
Pentachlorophenol	ND	50
All other acid semivolatile priority pollutants	ND	10

TABLE 22. (concluded)

Component	Concentration[a] (ppm, wt)	Detection limit (ppm, wt)	EP toxicity concentration limit (ppm)
Trace elements			
Antimony, Sb	ND	2	--
Arsenic, As	ND	1	5
Beryllium, Be	ND	3	--
Cadmium, Cd	ND	1	1
Chromium, Cr	ND	1	5
Copper, Cu	4[b]	1	--
Lead, Pb	1[b]	1	5
Mercury, Hg	ND	1	0.2
Nickel, Ni	1[b]	1	--
Selenium, Se	ND	1	1
Silver, Ag	ND	1	5
Thallium, Tl	ND	1	--
Zinc, Zn	ND	10	--

[a]ND denotes not detected; duplicate samples analyzed.
[b]Found in only one sample; not detected in the others.

SECTION 5

CONCLUSIONS

A series of incineration experiments was performed with the Vertac Chemical Company's toluene stillbottoms waste from trichlorophenol production. This waste is one of the more well known of the dioxin-contaminated wastes presently in existence. Samples of the waste tested in this study contained an average of 37 ppm 2,3,7,8-TCDD (37 µg/g).

Three incineration tests were performed during September of 1985. All were performed in the CRF rotary kiln incineration system with waste feedrate nominally 20 kg/hr.

With regard to the principal objectives of these tests, the following can be concluded:

- 2,3,7,8-TCDD DRE based on the combined extracts from the four MM5 trains at the vitual stack was greater than 99.99999 percent for one test. For the other test method detection limits prevented quantitating that better than 99.9998 percent DRE was achieved.

- Determination of particulate emissions at both the virtual and system stack could not accurately be determined due to technical and operational factors.

- Further research is needed to establish the amount, nature, and source of particulate emissions from these sources.

- HCl emissions in the virtual stack ranged from 0.2 to 0.45 kg/hr. These results are less than the RCRA standard of 1.8 kg/hr.

The above conclusions suggest that incineration should be considered a viable disposal method for this stillbottoms waste, given that appropriate safeguards are employed. The data in this study confirm that an incinerator, operating under proper conditions, is capable of achieving 99.9999 percent 2,3,7,8-TCDD DRE, with HCl emissions below the regulatory limit.

SECTION 6

QUALITY ASSURANCE/QUALITY CONTROL

The most critical QA objectives for this test series were dictated by the goal of the test series itself. This goal was to demonstrate incinerator capability to destroy dioxin-contaminted wastes or, more specifically, to demonstrate a DRE of at least 99.9999 percent for 2,3,7,8-TCDD.

The determinants of DRE are mass feedrate of the POHC in the influent waste (Q_{in}) and mass emission rate of the same POHC in the output stack gas (Q_{out}). Thus, it was on the measurement of these quantities that QC activities were most tightly focused during the CRF test series employing the toluene stillbottoms waste. In what follows, QC activities determine to the measurement of Q_{in} and Q_{out} will be listed, explained, and evaluated as regards their effectiveness in defining the quality of the measurements made. Such evaluations will be based on precision, accuracy, and completeness.

6.1 MEASUREMENT OF Q_{IN}

Waste was fed to the incinerator from a stirred reservior, connected to the feed pump with a flexible stainless steel line and mounted on the platform of a continuous weigh scale whose remote readout was located in the control room. Recordings of weight and clock time were taken at 10 to 30 min intervals throughout periods when feed was being pumped to the kiln. HRGC/LRMS analysis of preburn and inburn waste feed samples indicated the average concentration of 2,3,7,8-TCDD in this material to be 37 µg/g. Thus, measurements of elasped time, change in weight, and concentration constitute a complete set for calculation of Q_{in} during any recorded interval of waste feed. The continuous weigh scale was calibrated in duplicate with known weights yielding the result that its accuracy and precision were fixed by its reading resolution of ±0.23 kg (0.5 lb). Duplicate analyses of a waste feed sample for POHC concentration had duplicate results to two significant digits, suggesting a high order of precision for this measurement. As regards accuracy, surrogate recovery for these analyses averaged 92 percent while a standard analyzed with these samples yielded 115 percent recovery.

6.2 MEASUREMENT OF Q_{OUT}

Measurements of mass emission rates of 2,3,7,8-TCDD in the flue gas at various points in the CRF rotary kiln system were accomplished by extracting known volumes of this gas using MM5 sampling trains equipped with heated filters and XAD-2 absorbent. Extracts were prepared from each component of a

given train (probe, filter and holder, sorbent, condensate catch, and connecting lines), pooled, subjected to preliminary cleanup, and analyzed for 2,3,7,8-TCDD by HRGC/LRMS. Stack gas flowrate was measured by pitot tube as well as helium dilution.

The accuracy, precision, and completeness of stack gas sample volume measurements are supported by written calibration procedures and documentation of most recent calibration of equipment used to make these measurements. Method 5 data sheets, which are maintained for each sample taken, record additional information used to calculate sample volumes and to ensure the validity of sample taken. For example, barometric pressure and meter temperature used for the former and resin temperature for the latter.

Contamination of sample extracts from glassware and reagents as well as cross-contamination among trains may be severe problems when POHC determinations at the nanogram level are required to support DRE calculations on the order of 99.9999 percent. Possible contamination from glassware, reagents, and sample processing was monitored by submitting the extract harvested from a field blank train, along with extracts from the flue gas sampling trains for a given burn day, for POHC analysis. This field blank train was assembled by the sampling crew on each burn day and included all typical train elements (probe, filter and holder, adsorbent, condensate catch and connecting lines) except pump and meter box. In an effort to minimize cross-contamination among trains, several practices were adopted:

- All samples from one burn cleared the laboratory before another burn was undertaken
- All the glassware used to assemble a train as well as to process the sample extract harvested from it, constituted a unique set and were always used together to take samples from the same incinerator locations
- A given train was processed from receipt in the laboratory to the finished extract by one and only one worker

Three mechanisms were used to monitor accuracy of POHC analysis in flue gas samples:

- Use of a field spike train
- Inclusion of POHC surrogates in every sampling train
- Analysis of method standards with each batch of samples

The field spike train is identical with a field blank train with the addition of a 20-ng or 200-ng spike of native (unlabeled) 2,3,7,8-TCDD placed on the adsorbent (200 ng) or split between the adsorbent (10 ng) and the impinger condensate catch (10 ng). The 20-ng spike was recovered at 70 percent while the 200-ng spike yielded 10 percent and 98 percent recovery, respectively. The second monitoring mechamism, use of surrogates, was implemented by

placing 50 ng of $^{13}C_{12}$-2,3,7,8-TCDD and 10 ng of $^{37}Cl_4$-2,3,7,8-TCDD in the XAD-2 bed of each MM5 sampling train just prior to harvesting an extract for analysis from that train. Recoveries for the $^{13}C_{12}$-2,3,7,8-TCDD in all flue gas samples ranged from 12 to 104 percent with an average of 34 percent as shown in Table 23. Table 23 also shows that recoveries of the $^{37}Cl_4$-2,3,7,8-TCDD surrogate relative to the internal standard ($^{13}C_{12}$-2,3,7,8-TCDD) ranged from 93 to 144 percent with an average of 114 percent.

It should be emphasized that native (unlabeled) TCDD spiking and labeled surrogate spiking are overall recovery measures in that they measure the performance of the entire process of harvesting an extract from the sampling train, through preanalysis cleanup of the extract, through GC/MS quantitation of the compounds of interest.

The final accuracy monitor employed was the analysis of a method standard, prepared in the GC/MS laboratory, with each batch of incinerator samples. The recovery of this standard measures the performance of the preanalysis cleanup method as applied to a pure analytical grade standard solution. The results for these standards were 111 percent, 44 percent, and 159 percent recovery in three trials.

TABLE 23. SURROGATE RECOVERIES IN THE ANALYSIS OF MM5 TRAIN EXTRACTS

Sample	$^{13}C_{12}$-2,3,7,8-TCDD recovery (percent)	$^{37}Cl_4$-2,3,7,8-TCDD recovery (percent)
September 4, 1985 MM5 trains		
Kiln exit 1	21	110
Kiln exit 2	35	117
Afterburner exit 1	62	119
Afterburner exit 2	25	117
E-duct bottom	36	116
E-duct top	31	93
E-duct right	44	111
E-duct left	37	110
Stack east	48	108
Stack south	43	117
September 9, 1985 MM5 trains		
Kiln exit 1	60	113
Kiln exit 2	31	118
Afterburner exit 1	18	133
Afterburner exit 2	17	121
September 20, 1985 MM5 trains		
Kiln exit 1	37	116
Kiln exit 2	33	119
Afterburner exit 1	26	109
Afterburner exit 2	34	119
E-duct bottom	35	111
E-duct top	43	118
E-duct right	104	116
E-duct left	31	117
Stack east	26	142
Stack south	12	106
September 21, 1985 trains		
Kiln exit 1	44	119
Kiln exit 2	41	113
Afterburner exit 1	15	123
Afterburner exit 2	14	116
E-duct bottom	19	144
E-duct top	16	136
E-duct right	19	115
E-duct left	37	129
Stack east	21	111
Stack south	37	113
Average	34	114

SECTION 7

HEALTH AND SAFETY

The procedures followed during these tests, which were designed to protect the CRF staff and the nearby general population, were as documented in the test protocol document (5). As part of these procedures, several environmental ambient air samples were taken during the course of the test program, specifically aimed at measuring ambient dioxin levels both in the incinerator room and on the facility grounds.

Incinerator room air sampling was performed at a location in the southwest corner of the incinerator high bay area as shown in Figure 16. Sampling was performed during these time periods: for an almost 12-hour period on September 4, 1985, encompassing the blank burn test; for an almost 55-hour period beginning September 16 and ending September 19 while unsuccessful attempts were being made to conduct the full test burns; and for a 40-hour period beginning September 20 and ending September 22, encompassing the two full-burn tests.

All sampling was performed by pulling incinerator room air through an XAD-2 resin cartridge. A standard MM5 train glass resin cartridge containing 17g of resin was used for the September 4 sampling. For the sampling periods beginning September 16 and September 20, the resin cartridge consisted of a glass drying tube filled with a comparable amount of XAD-2 and held in place with glass wool plugs. Sampling on September 4 and the period beginning September 16 was at 4 L/min. Sampling for the period beginning September 20 was at 20 L/min.

After sampling, the resin was extracted and extracts concentrated, run through a cleanup procedure, and analyzed for 2,3,7,8-TCDD by GC/MS by the same procedures noted in Section 3.2 for flue gas MM5 train samples.

Ambient air sampling was performed during about the same 40-hour period beginning September 20 that the final incinerator room and sampling effort occurred. This period encompassed the full test burn period. The ambient air sampling methodology used was in accordance with that developed by the New York State Department of Health and demonstrated in the Binghampton Office Building. In this method, ambient air is pulled through a two-stage sampling device consisting of a 47-mm glass fiber filter and a glass resin cartridge charged with 8g of silica gel. Preassembled devices, prespiked with dioxin surrogates, were obtained from Battelle-Columbus Laboratories for use. Samplers were placed at two locations near the CRF, illustrated in

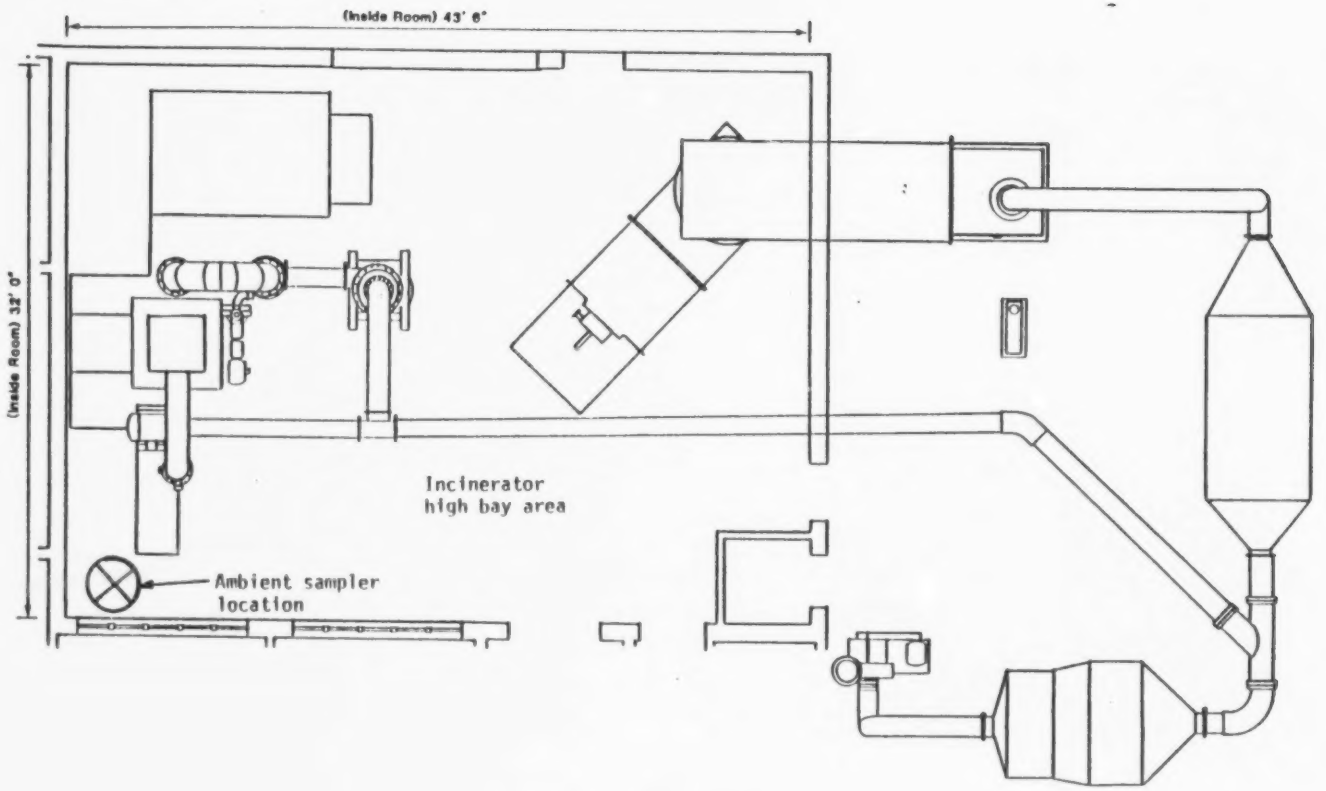


Figure 16. Ambient sampler location in the incinerator high bay area.

Figure 17. Sampling was performed at 20 L/min for the duration of the sampling period.

After sampling, the preassembled devices were returned to Battelle for PCDD and PCDF analysis. The analytical procedure used was a Battelle modification to the EPA Region VII protocol, "Determination of 2,3,7,8-TCDD in Soil," (1983). In this method the filter and sorbent resin are extracted with benzene and the extracts concentrated, run through several extract cleanup steps, then analyzed for tetra-CDD, penta-CDD, hexa-CDD, hepta-CDD, octa-CDD, tetra-CDF, penta-CDF, hexa-CDF, octa-CDF, 2,3,7,8-TCDD, and 2,3,7,8-TCDF by HRGC/HRMS.

Results from the incinerator room (high bay area) samples are shown in Table 24. As noted in the table, measured high bay ambient air 2,3,7,8-TCDD levels were nondetectable during the blank burn and full test burn periods. However, during the final test preparation period (September 16 through 19), the quantity of 2,3,7,8-TCDD detected in the extract sample normalized by the volume of air sampled would correspond to an ambient concentration of 9.2 ng/m^3.

This result is not surprising in retrospect. The final days prior to successful performance of the full burns were a period of intense activity in the incinerator room. During this time a few minor waste spills and leaks occurred as waste feed systems problems were being attacked. Although these were rapidly cleaned up, it is likely that some contaminated fugitive dust particles existed in the ambient air for some periods of time. These are the most likely source of the dioxin accumulated in the room air samples. Of course, all personnel working in the high bay area during this time were in Level B protective clothing, complete with respirator and face shields, so direct worker exposure would not have occurred.

Results from the outside ambient air samples obtained during the full test burn period are summarized in Table 25. As shown in the table, no tetra- (including 2,3,7,8-tetra), penta-, or hexa-CDDs or CDFs were found at levels above detection limits in any of the ambient air samples or blank samples analyzed. Total hepta-CDD was found in both ambient air sample cartridges, but comparable levels were found in the blank cartridges. Levels of total octa-CDD, hepta-CDF, and octa-CDF in the sample resin cartridge at location 2, the one furthest from the incinerator stack, were detected, but again comparable levels were found in the blank cartridges.

The only results for which sample levels were possibly significantly greater than blank levels were total octa-CDD and hepta- and octa-CDF for sampling location 1 (just below the incinerator's stack). The data in Table 25 suggest that the ambient air at this location may have contained an average concentration of about 50-pg/m^3 total octa-CDD, (blank cartridge value taken to correspond to 40 pg/m^3), 0.2 pg/m^3 of total hepta-CDF (blank value taken to correspond to 0.35 pg/m^3), and 1-pg/m^3 total octa-CDF (blank cartridge value taken to be zero, all blanks were nondetectable).

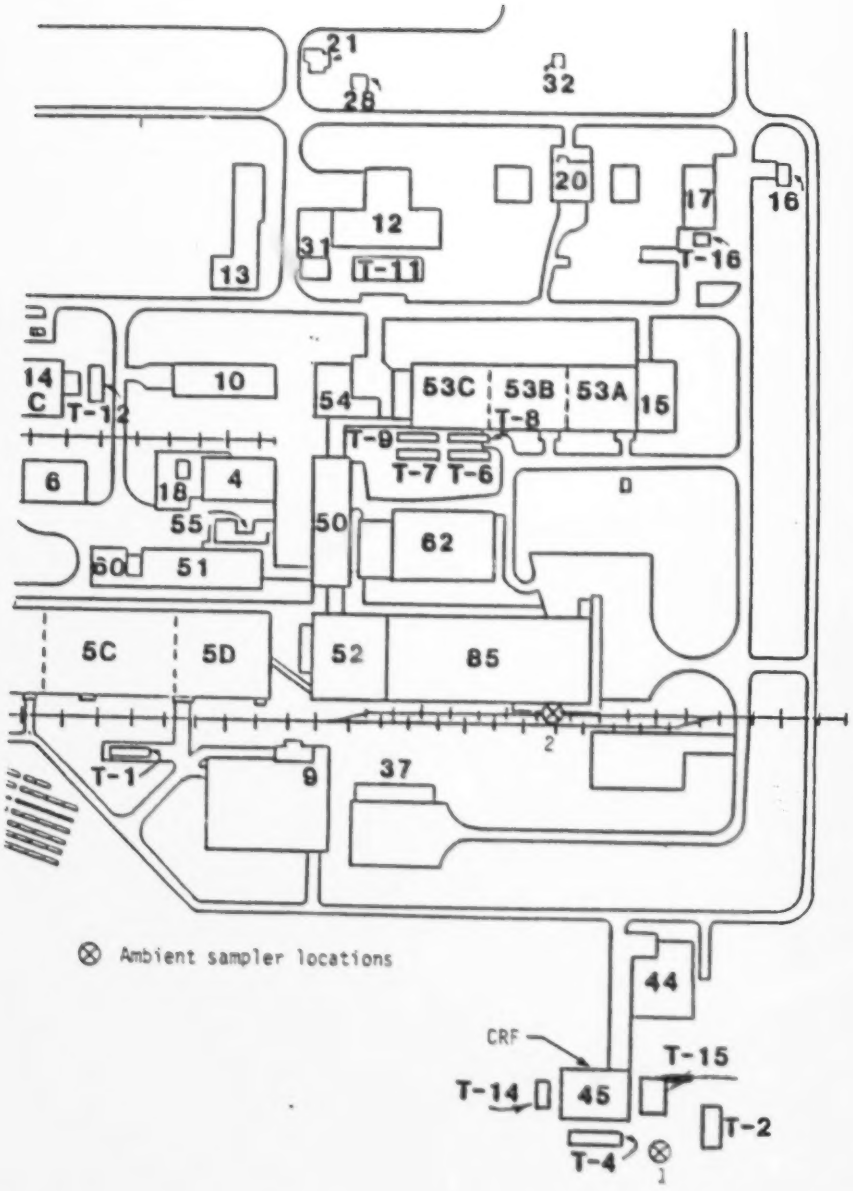


Figure 17. Outdoor ambient sampler locations during the Vertac waste burns.

TABLE 24. INCINERATOR ROOM AMBIENT AIR SAMPLING RESULTS

Time period	Start date:time to stop date:time	Sampling rate (L/min)	Volume sampled (m^3)	2,3,7,8-TCDD concentration (ng/m^3)
Blank burn	9/4/85:0950 to 9/4/85:2135	4	2.82	<1.3[a]
Final test preparations	9/16/85:0740 to 9/19/85:1425	4	18.9	9.2
Full test burns	9/20/85:1700 to 9/22/85:0250	20	40.6	<0.2[a]

[a]< = Numbers denote less than minimum detection limit of the analysis methodology for the appropriate sample analyzed.

TABLE 25. OUTSIDE AMBIENT AIR SAMPLING RESULTS

Parameter	Laboratory method blank (pg/m^3)	Blank filter/ resin[a] (pg/m^3)	Blank filter/ resin[a] (pg/m^3)	Sampling location 1[b] (pg/m^3)	Sampling location 2[b] (pg/m^3)
2,3,7,8-TCDD	<0.047	<1.0	<1.1	<0.95	<0.77
Total tetra-CDD	<0.047	<1.0	<1.1	<0.95	<0.77
Total penta-CDD	<0.10	<1.1	<0.28	<0.58	<0.20
Total hexa-CDD	<0.044	<0.71	<0.17	<0.43	<0.18
Total hepta-CDD	<0.86	9.2	4.5	9.9	4.5
Total octa-CDD	<1.7	41	40	90	41
2,3,7,8-TCDF	<0.053	<0.89	<0.20	<0.28	<0.20
Total tetra-CDF	<0.053	<0.89	<0.20	<0.28	<0.20
Total penta-CDF	<0.040	<0.44	<0.067	<0.24	<0.11
Total hexa-CDF	<0.027	<0.58	<0.10	<0.26	<0.072
Total hepta-CDF	<0.86	<1.5	0.35	0.57	0.27
Total octa-CDF	<1.7	<6.3	<0.38	0.98	<0.21

[a]Two preassembled sampling devices were submitted as trip blanks.
[b]See Figure 7-2.

The total measured CDD plus CDF from the above, thus was about 50 pg/m^3. The preliminary risk assessment included in the test protocol document (5) for these tests noted that current data suggest that an increased lifetime cancer risk of 1 in 10^4 would be associated with continuous lifetime exposure to ambient levels of 2,3,7,8-TCDD of 10.3 to 31.5 pg/m^3. If all isomers of all PCDDs and PCDFs analyzed were considered to be as carcinogenic as 2,3,7,8-TCDD (a very conservative assumption), then a 50-pg/m^3 total ambient level would be associated with increased lifetime risk from continuous lifetime exposure of between 1.6 in 10^4 and 5 in 10^4.

REFERENCES

5. "Protocol for an Incineration Study of 2,4,5-T Stillbottoms with TCDD Contamination," prepared by Versar, Inc., Southern Operations for EPA/HWERL, Combustion Research Facility, July 1985.